INVESTIGATION OF LEAD AND ZINC DISPERSION FROM AN ABANDONED MINE SITE AT TYNDRUM, SCOTLAND

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By

Nurlidia Mansor

MSc (Environmental Engineering)

BSc (Biotechnology)

Department of Environmental Chemistry

Faculty of Physical Science

University of Glasgow

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DEDICATION

To my grandmother,

brilliant, inspiring

women of substance…

Siti Khadijah Abdul Rahim

1900 - 1994

ABSTRACT

This research focuses on atmospheric and fluvial dispersal of Pb and Zn from an abandoned mine at Tyndrum, Scotland, which potentially acts as a significant source of contamination to the surrounding area. Concentrations of Pb and Zn in tree bark samples and peat profiles were measured to assess aerial deposition and fallout around the main mine site. Dispersal of contaminants through fluvial transport was assessed by analysis of river water and sediment on site and in the main river system draining the area, extending 25 km downstream from the mine area. Attempts were also made to determine whether the contamination is due to contemporary dispersal of material from the abandoned mine waste dumps, or originates from past deposition. Pb and Zn concentrations in tree bark from Scots pine (*Pinus sylvestris*) were high, but decreased with increasing distance up to approximately 100 m from the main dumpsite. Concentrations reduced markedly beyond this distance, possibly owing to the density of the forest stand. It is suggested that tree bark samples provide a useful medium for monitoring and quantifying contemporary aerial dispersal. Distributions of Pb and Zn within peat soil profiles provide information of past atmospheric deposition. Subsurface peaks of Pb and Zn can be linked to the period when mining was active during the 19^{th} and early 20^{th} centuries using the ^{210}Pb dating method. The dispersal of Pb and Zn within the fluvial system was assessed by measuring concentrations of the contaminants in the solution, suspended particle and bed sediment phases. It was found that Pb and Zn are mainly transported in suspension in the 1.2-53 μm suspended sediment fraction and are consequently deposited throughout the dispersion pathway in riverbed, lake and riverbank sediments. The contaminant Pb in an overbank core was confirmed as originating from the Tyndrum mine on the basis of its $^{206}Pb/^{207}Pb$ isotope ratio characteristics. This confirms a previous hypothesis that waste from the mine is an important contributor to Pb contamination over the entire length of the river system as far as Loch Tay. Thus overall, the investigation concludes that although the atmospheric dispersal of the contaminants is mostly contained within the vicinity of the Tyndrum main mine, the fluvial system remains a significant pathway for dispersal of Pb and Zn from the Tyndrum waste and that the presence of these metals within the river may persist for many years to come.

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AUTHOR'S DECLARATION

Except where specific reference is made to other sources, the work presented here is the original work of the author. It has not been submitted, in part or in whole, for any other degree. Some of the results may have been published elsewhere.

Nurlidia Mansor

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ABBREVIATIONS

AAS	Atomic Absorption Spectroscopy
ICP-MS	Inductively Coupled Plasma Spectroscopy
SEM	Scanning Electron Microscopy
LOI	Lost On Ignition
CEC	Cation Exchange Capacity
CIC	Constant Initial Concentration
CRM	Certified Reference Materials
MWD	Main Waste Dump
SSD	Small Side Dump
Pb	Lead
Zn	Zinc
NW	Northwest
SE	Southeast
SSSA	Soil Science Society of America
APHA	American Public Health Association
DOE	Department Of Environment, Malaysia
FAO	Food and Agriculture Organisation
FRIM	Forest Research Institute Malaysia
SUERC	Scottish Universities Environmental Research Centre
WHO	World Health Organisation

CHAPTER ONE

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1.0 INTRODUCTION

Over centuries, anthropogenic activities such as mining, metallurgical processes, burning of fossil fuels, industrial production and agricultural operations have resulted in extensive heavy metal contamination, which threatens the well-being of the global environment of today. The mining industry is amongst the major contributors that have caused considerable heavy metal contamination of land, rivers and air in many parts of the world (Nriagu & Pacyna (1988); Salomons (1995)).

Britain is no exception to the detrimental effects of mining. Mines throughout the country, whether active or derelict, have become a persistent source of heavy metal contamination. Tyndrum is one of many examples of mining areas in Britain that have been left desolated and polluted as a legacy of its past mining industry. Situated in central Scotland, the former mine at Tyndrum produced lead sulphide (galena) and zinc sulphide (sphalerite) as its main ores during its various phases of operation from the 18th century to the early 20th century (Pattrick (1983)). The derelict site has already been recognized in past studies as being highly polluted and waste from the site is suspected to be the probable source of heavy metal contamination to surrounding areas (MacKenzie & Pulford (2002)).

This research attempts to investigate the environmental transport pathways, which result in dispersion of lead and zinc contaminants from the abandoned mining site. Airborne deposition of the contaminants in the vicinity of the mine site was assessed from profiles of tree bark as well as peat cores. Fluvial transport of the contaminants was investigated in the river system which drains the main mine site and extends approximately 25 km downstream to Loch Tay, a lake in central Scotland. The investigation also included characterising the source of the contaminants by means of stable Pb isotope analyses and reconstructing past deposition using ^{210}Pb dating.

The overall investigation has the aim of providing a fundamental understanding on the extent and magnitude of heavy metal dispersal from the abandoned mine at Tyndrum. A short study on remediation efforts of an ex-mine in Malaysia was also included in this research as a brief outlook on land reclamation practices outside Britain.

1.1 The Tyndrum mine site

Tyndrum (OS NN 330303) is a small village located 70 km northwest of Glasgow in Scotland. It is strategically located at one of the major junctions in the Central Highlands of Scotland where roads from Glasgow divide north of the village towards Fort William (OS NN 103738) and Oban (OS NN 859298). In the 1800s however, Tyndrum established its recognition when it acquired two railways with two stations, Tyndrum Upper Station and Tyndrum Lower Station. As part of the renowned West Highland Line[1], the railway route also divides to serve Fort William and Oban as shown in Figure 1.1

Tyndrum is also situated along the popular West Highland Way[2], a long distance walking route of 152 km in length, stretching from Milngavie, north of Glasgow to Fort William. Although the Tyndrum village has a small population of 167 (Stirling Council, 2002)[3], this popular footpath attracts approximately 50,000 people every year giving tourism the present economic activity at Tyndrum.

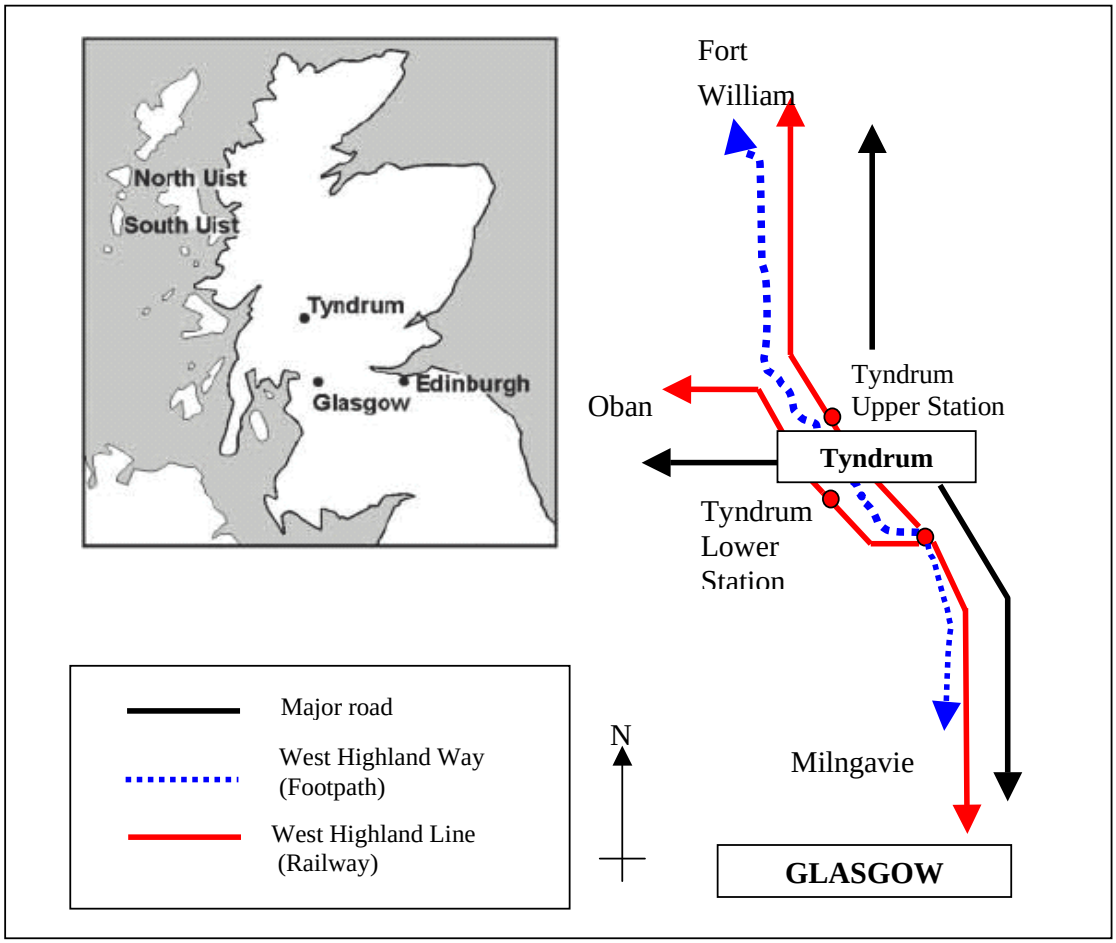

Figure 1.1: Map showing location of Tyndrum, Scotland (inset) and the West Highland Way and West Highland Line that passes through Tyndrum.

The name Tyndrum comes from “Tigh an Druim”, which means “the house on the ridge” in the native Scottish language, Gaelic. This ideally reflects the topography of the village, which sits on the ridge of the mountainous hills. It was in this hillside that the first mineral veins were discovered in the early 17th century on the west side of Tyndrum, turning the village into a significant mining centre at the time. Figure 1.2 shows the Tyndrum fault where the Pb and Zn mineral veins were found, visible from below in the valley. The area of metal pollution below the mine is clearly visible in the photo as the grey area, almost devoid of vegetation.

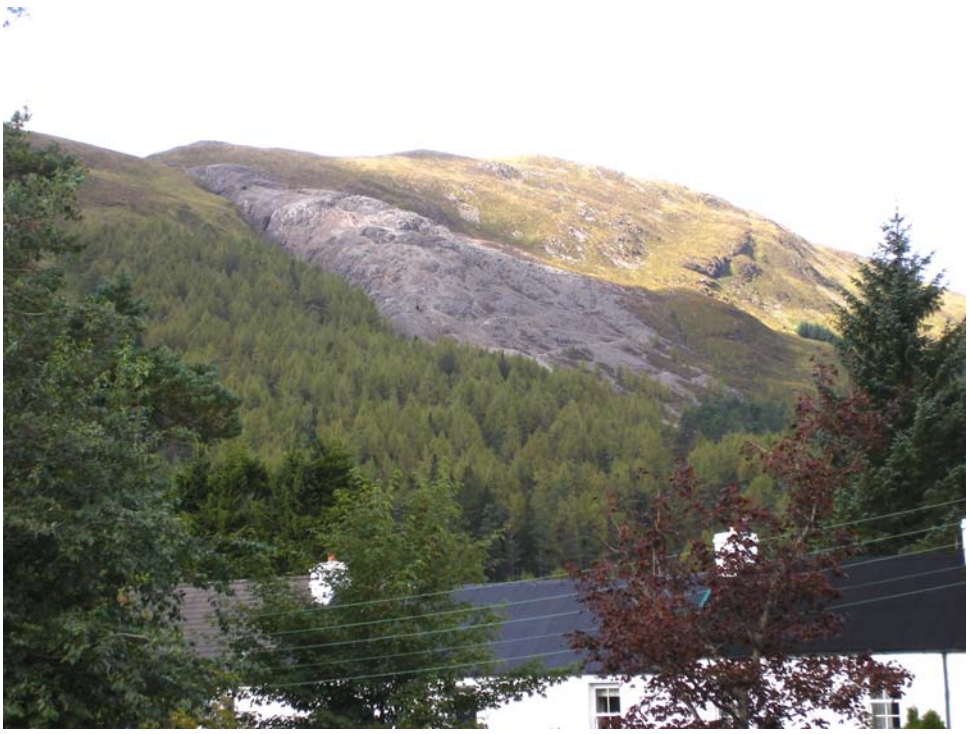

Figure 1.2: Photo of Tyndrum Fault as observed from the village.

As reported by Pattrick (1985), Tyndrum has many mineralised localities, which include the Pb and Zn veins. Figure 1.3 shows the veins situated in northerly trending fractures related to the Tyndrum fault where different vein types can be recognised over a distance of 80 m. The sulphide-bearing quartz veins to the west of the Tyndrum Pb/Zn mine were reported by Pattrick (1983) to contain about 4.32 oz ton^{-1} of Au. Although the village had a brief experience of a gold rush close to the Cononish Farm (Figure 1.3) the main attention and interest was in the mining of lead and zinc ores.

While past studies of the geology and geochemistry of the Tyndrum Pb/Zn mineralisation have been broadly documented by Curtis (1993); Pattrick (1985); Pattrick (1983), the current extent of residual environmental contamination from the mine has yet to be fully characterised. Between 1741 and 1862 approximately 20,000 tones of high grade ore was mined. Pattrick (1985) reported that after mining started to decline in 1862, the waste dumps were reworked between 1916 and 1925.

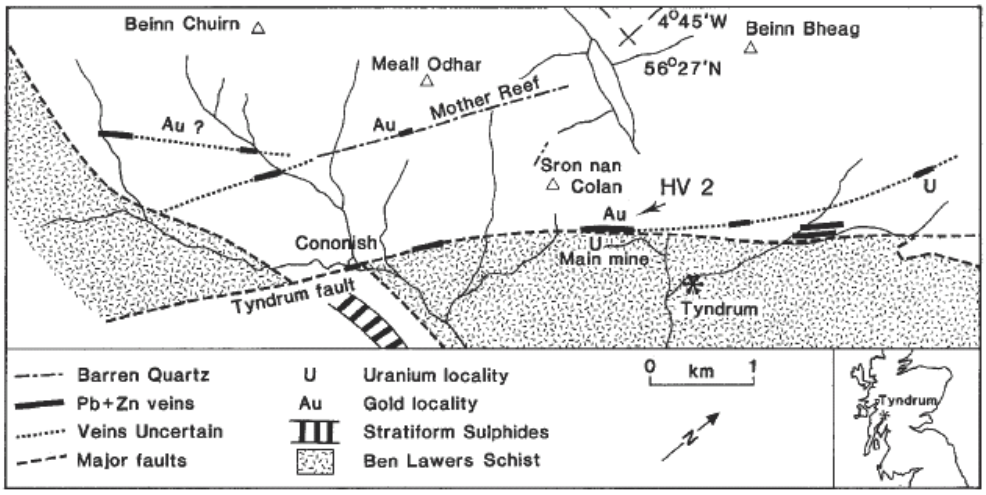

Figure 1.3: Mineralised localities at Tyndrum (Pattrick et al. 1985)

MacKenzie & Pulford (2002) provided archival environmental evidence of the reworking of the Tyndrum mine waste dumps via an analysis of Pb and Zn concentrations and stable lead isotope ratios in peat cores collected from the vicinity of the mine. High levels of Pb deposition in the core layers corresponding to the early 20th century on the basis of ^{210}Pb dating were consistent with the recorded period of reworking of the mine waste.

Evidence which suggests that the site continues to act as a source of contamination was provided by Farmer et al. (1997a), who found anomalously high concentrations of lead in sediments deposited in Loch Tay some 25 km away from the mine site. The pattern of Pb deposition in the ^{210}Pb-dated Loch Tay sediments corresponded to the history of mining and waste processing at Tyndrum. Moreover, the persistence of high Pb concentrations in the recently deposited surface sediments in Loch Tay indicated that the Tyndrum site probably remains an active contemporary source of contaminants through fluvial transport.

The isotopic composition of the deposited Pb was also found to be inconsistent with the general regional patterns of temporal variations of atmospherically deposited Pb. As will be explained in Chapter 2, most geological materials within the region have similar trends in response to the use of Pb from different sources.

In the study by Farmer et al. (1997a), the $^{206}Pb/^{207}Pb$ atom of 1.144 for Tyndrum Pb (Moorbath (1962)) was found to be consistent with the implication that Pb in Loch Tay sediments originates from Tyndrum mine waste.

The past workings of the mine offer an interesting challenge to investigate and evaluate the past and contemporary dispersal of contaminants within the site and beyond Tyndrum forms the central area of investigation in this research study.

1.1.1 Problem Identification

Alloway (1990) describes all contaminated or polluted situations as comprising the following components: a pollutant source, the pollutant itself, a transport mechanism by which the pollutant is dispersed and the receptor where the transport phase terminates. To begin with, the distinction between a contaminant and a pollutant needs to be clarified before identification of the problem is addressed.

Pollution is defined as a condition when contaminants cause a definite threat to humans and the environment. As further mentioned by Alloway (1990), the term pollution is usually used when toxicity has occurred. On the other hand, the term contamination is used in conditions where inputs may not appear to cause obvious harmful effects, although there is an increase in the concentration of a particular substance. Therefore, the term contamination was found to be more appropriate to be used in this study.

Following the above convention of Alloway (1990), the chief sources of contamination in this research are the waste dumpsites at the mine and the contaminants are lead (Pb) and zinc (Zn). The main transport routes are through atmospheric and fluvial dispersion, and characterisation of these processes is central to this research. The samples collected in this study are representatives of the receptors, which include tree bark, peat soil, river water, riverbed and riverbank sediments. By means of this identification, the site of interest can be evaluated in the context of its extent as a source of contamination towards the wider environment.

1.1.2 Research Objectives

The main objectives of this research were;

1. to investigate the extent of atmospheric dispersion of lead (Pb) and zinc (Zn) from the former mine using tree bark and peat soil samples;

2. to investigate the extent of fluvial dispersal of Pb and Zn from the main mine site using samples from the river system through its network downstream;

3. to determine whether the dispersal of contaminants from the former mine is historical, of contemporary origin or both;

4. to investigate atmospheric dispersal of contaminants at another former mine site located in Malaysia as a comparison to Tyndrum, as well as observing remediation work done at the site.

1.1.3 Significance Of Research

It was hoped that this research would provide information on the extent of contamination of the former mine towards its surrounding area. This is important as the Tyndrum former mine is within close proximity to the village, which is a local population centre providing market, tourism and transport facilities. The outcome of this research will assist in determining whether the former mine is cause for concern on possible health effects towards the local residents and the wider public.

This research also provides a significant prospect for future work in Malaysia. There are currently over 114,000 ha of former mine sites in Malaysia as a result of tin mining operations over the past century (Ang & Ho (1994)). Land reclamation and remediation work are often hampered by the lack of research activities and proper identification of the extent of contamination.

As a result, the former sites are used extensively for agriculture, aquaculture and growing crops regardless of potentially hazardous effect to human health and the environment (Ho et al. (2000); Mohd Osman & Ang (1999)). Research is presently conducted by the Forest Research Institute Malaysia (FRIM), to improve the site quality of tin tailings through remediation techniques such as planting forestry systems. As part of the present research, a two-month study was carried out at FRIM on a remediated site based on one of the research methods employed in the investigation at Tyndrum. Bark samples from timber species were used to quantify the extent of atmospheric dispersal of heavy metals on the remediated ex-mining sites. This initial study will hopefully be a start in contributing valuable and useful information and understanding in order to tackle the predicament of derelict land mines in Malaysia in the future.

1.2 Thesis Overview

Chapter 1: Introduction

This chapter introduces background information that is significant to the research. It also highlights the main issues that compel the research study. The main objectives of the research are presented and the chapter includes the practical significance of these aims. This chapter concludes by providing the basis or motivation for continuation of the research and also presents a discussion of the overall scope of the work.

Chapter 2: Literature Review

The second chapter of this thesis summarises the literature survey that has been conducted. It contains coverage of the main established concepts published in the literature concerning impact of anthropogenic metal releases to the environment, including those from former mines. An insight into the basis for investigation of fluvial and atmospheric dispersal is also highlighted.

Chapter 3: Sampling Site and Methods

The third chapter includes a description of the sampling site, the sampling procedures and the methodology applied in this research. It is divided into three separate sections. The first section describes the features of the sampling site in detail.
The second section clarifies the sampling techniques that were carried out on site as well as the sample preparation process in the laboratory. The final section in this chapter explains the procedures of all the laboratory analyses involved in this research study.

Chapter 4: Results and Discussion

This chapter presents all of the results acquired in this study. The results are separated into three sections according to the different samples; Tree Bark, Peat Core and River Water and Sediment. Each section is followed by discussion and explanations based on the results obtained.

Chapter 5: Case Study: Remediation of an ex-mining site at Bidor, Malaysia

The fifth chapter focuses on the case study conducted at a former tin mining site at Bidor, Malaysia. The two month study at the Forest Research Institute Malaysia (FRIM) provides an interesting comparison of the Tyndrum and Bidor former mine sites, which are different logistically but of a similar nature. The study involves observation on the remediation efforts using forestry systems. Samples of tree bark were analysed to evaluate the atmospheric dispersal on site. The result of the experiment is briefly discussed and summarised at the end of this chapter.

Chapter 6: Conclusions and Recommendations

The final chapter of this thesis presents the overall conclusions of the research that has been conducted. It is based on the findings and refers to the main aims and objectives of this research. Several recommendations are also included which hopefully will be useful and valuable for possible future work.

CHAPTER TWO

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2.0 BACKGROUND AND LITERATURE REVIEW

This chapter summarises the literature study that has been conducted. It includes coverage of the literature of the main concepts concerning impacts of heavy metals from anthropogenic sources on the environment. It focuses on the effects of abandoned mines and their persistent contaminant contribution via atmospheric and fluvial dispersal to their surroundings.

2.1 Heavy Metals in the Environment

Heavy metals can be found in varying amounts in the environment, whether in soil, water, sediments, or plants. Originating from the natural component of the earth's crust, heavy metals are released naturally to the environment through weathering of rocks and soils as mentioned by Alloway (1990); Dill (2001); Galloway et al. (1982); Lantzy & Mackenzie (1979). Other sources include: the decomposition of plant and animal detritus; precipitation or atmospheric deposition of airborne particles from volcanic activity, wind erosion, forest fire smoke; plant exudates; and oceanic spray (Galloway et al. (1982); Schulz & Schulz (2000)).

Heavy metals are widely known as the large group of elements with a density greater than 6 g cm^{-3} as explained by Alloway (1990) and Miller (1997). Metals are natural and, in large part, essential components of the global ecosystems. Other alternative terms such as 'trace metals' and 'trace elements' are also widely used to show that minute amounts of these heavy metals such as copper, iron, selenium, zinc are essential to preserve the metabolism of living organisms. However, excessive amounts of these metals can have damaging effects and pose a health risk to humans and to the environment (Alloway et al. (1984); Harrison (2001); Jung & Thornton (1997); Schulz et al. (1999)). Some metals such as lead and mercury are not known to perform any useful biochemical function. Human activities simply redistribute metals within and between ecosystems (Allan (1997)).

The term 'potentially toxic elements' (PTEs), are also used regularly in literature to refer to elements that are known to be potentially toxic at elevated concentrations. Lead, zinc, copper, cadmium, arsenic and nickel are amongst elements that are regularly referred to as PTEs (Dudka & Miller (1999); Galan et al. (2003); Wilkinson et al. (2001)). Due to the variety of terms available in literature, the term 'heavy metals' is found to be the most appropriate to be used in this study.

Heavy metals are also released as a consequence of human activities such as fossil fuel combustion and industrial processes. Since the start of the Industrial Revolution in the late 18^{th} century, the amount of heavy metals in the environment from natural sources has been greatly exceeded by heavy metal emissions from anthropogenic sources. For example, the industrial revolution initiated a change from wood, as a dominant source of fuel, to coal and the impact of coal mining: refining and combustion processes introduced considerable amounts of heavy metal emissions to the environment.

In the earlier periods of the industrial revolution, the rate of emission from anthropogenic sources was relatively low, due to the low volatility of most metals. Within the last century however, the introduction of high temperature technology in the processes of smelting and fossil fuel combustion has increased the rate of release for some metals considerably.

Galloway et al. (1982) made an assessment to determine whether man or nature controls current concentrations of heavy metals in the environment by comparing anthropogenic activities against natural emission processes. Using the Mobilization Factor (MF) as shown in Equation 1, the study found that heavy metals are enriched in the atmosphere by anthropogenic emissions in the order of Pb>Ag>Sb,Mo>Zn,Cd>Cu>Sn>V,As,Se,Ni>Cr>Mn,Co,Hg. Table 2.1 shows the global MF factors from annual emission rates.

$$MF = \frac{\text{Emission rate from human sources}}{\text{Emission rate from natural sources}}$$

Equation 1: Mobilization Factor (Lantzy and Mackenzie, 1979)

Table 2.1: Global Mobilization Factors (MF) based on annual emission rates (Galloway et al., 1982)

	Emissions (10^8 g y^{-1})		Mobilization
	Natural	Anthropogenic	Factor (MF)
Antimony (Sb)	9.8	380	39
Arsenic (As)	28	780	28
Cadmium (Cd)	2.9	55	19
Chromium (Cr)	580	940	19
Cobalt (Co)	70	44	0.63
Copper (Cu)	190	2600	14
Lead (Pb)	59	20,000	340
Manganese (Mn)	6100	3200	0.52
Mercury (Hg)	0.40	110	275
Molybdenum (Mo)	11	510	46
Nickel (Ni)	280	980	3.5
Selenium (Se)	4.1	140	34
Silver (Ag)	0.6	50	83
Tin (Sn)	52	430	8.3
Vanadium (V)	650	2100	3.2
Zinc (Zn)	360	8400	23

Note: Natural Emissions = soil dust + volcanic dust and volcanic emanation fluxes
Anthropogenic Emissions = fossil fuel and industrial particulate fluxes

Another method of assessment is by comparing the ratios of Al-normalised metal concentrations in the atmosphere to corresponding Al-normalised crustal, known as the Enrichment Factor (EF)

$$\text{Enrichment Factor (EF)} = \frac{[Me]/[Al]_{air}}{[Me]/[Al]_{crust}}$$

Equation 2: Enrichment Factor (EF)

If EF > 1, a metal Me is enriched in the atmosphere relative to its concentration in the earth's crust, implying a source other than the crust. If EF = 1, Me is not enriched in the atmosphere, implying a crustal source.

The spread of industrialization throughout the world has substantially increased the anthropogenic impact of heavy metals on the environment. Thus, assessment of the current level of heavy metal contamination by anthropogenic sources is essential to establish an accurate and complete emission inventory on a global scale. It is carried out to consider the current level of environmental contamination by heavy metal pollutants, major emission sources and source regions, and the contribution of the atmospheric pathway to the contamination of terrestrial and aquatic environments (Alloway (1990); Pacyna & Pacyna (2001)).

2.1.1 Anthropogenic Impact and Assessment

Industrialisation, coal burning, mining and smelting, and the combustion of fossil fuels are amongst the anthropogenic or man-made activities that are emitting high levels of heavy metals in the global environment. Archaeological evidence suggests that the earliest human exploitation of heavy metals was copper smelting, which can be traced back to around 7000 BC and that the widespread environmental impacts of metallurgy were felt in many parts of the world in prehistoric times, particularly as a result of timber felling for smelting (Tylecote et al. (1983)).

As previously mentioned, the Industrial Revolution has caused the production of heavy metals such as lead, copper, and zinc to increase exponentially. As discussed by Nriagu (1996), between 1850 and 1990, production of these three metals increased nearly 10-fold, with emissions rising in parallel due to the high demand for metals. Figure 2.1 illustrates the comparison of emissions with the mine productions of Cu, Pb and Zn where 90% of the mine outputs were utilized within this century. Once emitted, metals can reside in the environment for hundreds of years or more.

Evidence of human exploitation of heavy metals has also been found in ice cores in Greenland and seawater in the Antarctic. The lead content of ice layers deposited annually in Greenland shows a steady rise that parallels the mining renaissance in Europe, reaching values 100 times the natural background level in the mid-1990s.

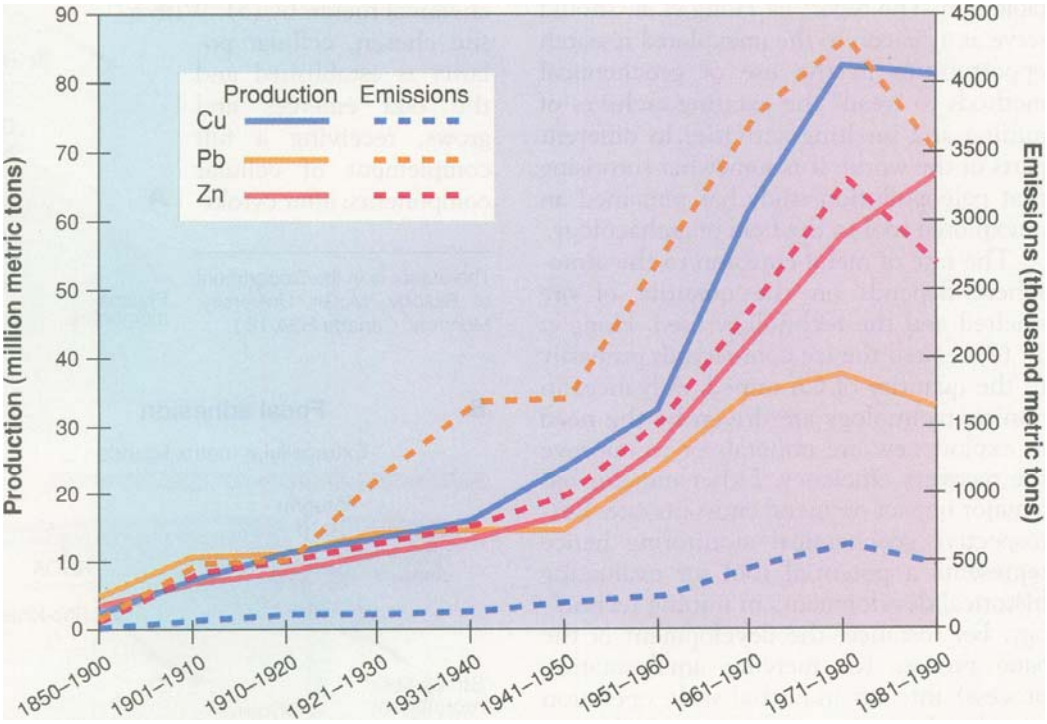

Figure 2.1: Recent historical changes in mine production and anthropogenic emissions of trace metals to the atmosphere (Nriagu 1996)

Since Nriagu & Pacyna (1988) made the first global emission estimate for heavy metal pollutants, major progress has been made in assessing emissions of trace metals in various countries and even regions such as in Europe. Alloway (1990) estimated that there are between 50,000 and 100,000 contaminated sites in the United Kingdom, occupying around 3,000,000 ha. In August of 2005, the Environment Authority issued a report under the Act on "Indicators for Land Contamination" in England and Wales which stated that amongst 325,000 industrial sites, 33,500 sites were identified as potentially contaminated, 21,500 sites were potentially requiring remediation and 280 sites were formally established as contaminated. Assessments such as these will without doubt promote greater understanding of the environmental impact and give rise to stringent policies in managing and controlling recent environmental situation.

Pacyna & Pacyna (2001) reported an assessment of global and regional emissions of trace metals from anthropogenic sources worldwide. One of the conclusions included was that the combustion of leaded and low-leaded gasoline continues to be the major source of atmospheric Pb emissions. The largest anthropogenic emissions of atmospheric trace metals were estimated to be in Asia due to the growing demands for energy in the region and increasing industrial production. While Europe and North America show decreasing tendency over the last two decades, the increasing emissions in Asia show a lack of efficiency in emission control and fewer environmental policies. This proves the importance and effectiveness of environmental management and control in tackling the impact of heavy metals from anthropogenic sources.

2.2 Environmental Impact of Mining

Mining is one of the main contributors of heavy metal contamination worldwide. Mining and smelting of ore-bearing rocks can release large quantities of trace element bearing volatile species and dust particles into the environment (Merrington & Alloway (1994a); Thornton (1996)).

Mining has resulted in environmental releases of a wide range of metals, especially As, Cd, Cu, Ni, Pb and Zn. As Nriagu and Salomons (Nriagu & Pacyna (1988); Salomons (1995)) point out, mining in itself affects relatively small areas. The main problems are the tailings and waste rock deposits of the mining area. Tailings may also give rise to acid mine drainage (AMD), caused by the presence of surplus oxygen in mine deposits that contain sulphides. AMD can contain elevated levels of metals, which may leach into rivers giving rise to a wider dispersion of metals both in solution and particulate form.

As Merrington & Alloway (1994a) explains that ore bodies generally include a range of minerals containing both economically exploitable metals (in ore minerals) and uneconomic elements (in gangue minerals). As a result, large amounts of waste are produced during mining because the ore is only a small fraction of the total volume of the mined mineral. Allan (1997) describes the typical metal mine as using more water by weight in production of the metal concentrate than the weight of the ore grade material itself. Water losses and water gains at a typical metal mine show that the main direct release of metals is from tailings and polishing ponds. Thus, mining and milling and disposal of tailings, along with mill wastewater, provide obvious sources of contamination (Monna et al. (2004)).

The process of smelting of ore concentrates could also result in greater release of metals to the atmosphere than the mining activities themselves (Nriagu & Pacyna (1988)). Smelters such as the ones in Canada (Adamo et al. (1996);Freedman & Hutchinson (1980)) and Avonmouth, UK (Harrison et al. (1993)), have been found to cause severe heavy metal contamination within their surroundings. Freedman & Hutchinson (1980) found contamination of forest soils, soil litter and vegetation deposited within a 60 km radius from the Sudbury nickel-copper (Ni-Cu) smelter. Nriagu et al. (1982) found accumulation of Ni, Zn and Pb at 100-600, 10-60 and 5-30 mg m^{-2} y^{-1} in lake sediments collected within 30-km radius of the Sudbury Ni-Cu smelter. The study further reveals the absence of heavy metal accumulation in surface sediments, which suggests previously stored contamination might have been leached.

Nriagu & Pacyna (1988) concluded that each year, millions of tonnes of 'new' trace metals are produced from mines and are subsequently redistributed in the biosphere. The greatly increased circulation of toxic metals through the soils, water and air and their transfer to the human food chain remains an important environmental issue, which entails some unknown health risks for future generations.

The dispersal of heavy metals from mining activities and its processes are evidently causing severe consequences towards the environment. The current study however, focuses into the dispersion from former mine sites that experiences dispersal from its abandoned waste spoils. Dispersion can occur over hundreds of kilometres if control measures are not carried out, as often observed in the past (Moore et al. (1991)). Mining practices in the past have resulted in dire environmental impacts due to ineffective mining processes as well as lack of stringent environmental policies.

Birch et al. (2001) found that sediment in a creek flowing through a country town near Sydney, Australia had markedly enriched Cr, Pb and Zn concentrations over background levels. This was partly due to a contribution from a long history of metal-based industry. In the Lot-Garonne River, France, the fluvial system is known for its historic heavy metal pollution resulting from mining and smelting activities since the late 19^{th} century. The reservoir sediments in this area have recorded historical trends in deposition of Cu, Zn, Cd and Pb, establishing a connection between the temporal evolution of the heavy metal profiles and historical changes in smelting and waste-treatment proceedings (Audry et al. (2005)).

Johnson et al. (1994) reported that past mining activities used simple and inefficient processing technology when recovering the desired metals compared with the more recent processes of magnetic, gravity and floatation recovery process. As a consequence, the waste materials from past mining operations contain high residual quantities of toxic metals. These abandoned and derelict mines are often found to have waste materials in excess of 1% by weight of elements such as lead and zinc.

Table 2.2 summarises the concentrations of principal base metals copper, lead and zinc found in spoils from various parts of Britain taken from the study.

Table 2.2: Concentration of Cu, Pb and Zn from abandoned mines in Britain. Johnson et al. (1994)

Mining region	Counties	Number of sites surveyed	Principal base metals		
			Cu (mg kg^{-1})	Pb (mg kg^{-1})	Zn (mg kg^{-1})
S. W. England	Devon and Cornwall	16	65-6140	48-2 070	26-1 090
W. and N.W. England	Shropshire and Cheshire	12	15–7260	840–26 000	980–21 000
N. Pennines	N. Yorkshire and Durham	8	20-140	605-13 000	470-28 000
S. Pennines	Derbyshire	17	23-97	10800-76500	127000-42000
Lake District	Cumbria	7	77-3800	2070-7360	4690-7370
Mid-Wales	Powys and Dyfed	10	67-195	1670-54000	475-8000
N. Wales	Clwyd and Gwynedd	19	30-5750	6400-76000	11300-12700
S.Scotland	Dumfries and Galloway	6	125-657	4730-28300	1600-31400
Normal agricultural soil			2-100	2-200	10-300

Former mine sites that have been left derelict and abandoned continue to be a threat to the environment, worldwide. The current study focuses on the impact of an abandoned and derelict mine at Tyndrum, in central Scotland, as well as a case study from a mine site at Bidor, Malaysia. Previous studies and records of the impact of former mines in Malaysia on the environment are fairly limited and poorly documented. A brief review of the mining situation will be discussed in Chapter 5.0.

2.2.1 Monitoring and Assessment

Monitoring and assessing the impact of mines, whether active or derelict, are essential in order to address potential health risks for humans, wildlife, and plants. Monitoring studies can be focussed on the source of contamination, along the dispersion pathway or at its final destination/receptor. In some cases, studies involve assessing and comparing monitoring data representative of all three components to evaluate the status of a particular contaminant of interest. As mentioned by Wolterbeek (2002), in the case of air pollutants, information can be obtained by dispersion modelling, which is source-oriented, and by field measurements of the receptor or effect-orientation.

In the case of evaluating the impact of a derelict or abandoned mine, distinguishing the possible emission pathways of the contaminants and their eventual fate is imperative in acquiring an effective and comprehensive assessment. The Source-Pathway-Receptor assessment depicts the substance from the mine site as the 'source'. The 'pathway' is how the contaminant reaches and affects the receptor. This is through various possible environmental transfer pathways, which include aerial dispersal and fluvial transport. 'Receptors' are whatever are being contaminated, such as soil, air, and water and even humans.

Figure 2.2 illustrates Salomons (1995) description of the pathway, whereby metals initially released by mining activities, will eventually be deposited in various compartments of the surface layer of the earth. Over time, the metals released through the atmosphere or into the waterways will end up as diffuse contaminants in soils and sediments or discarded with wastes at disposal sites.

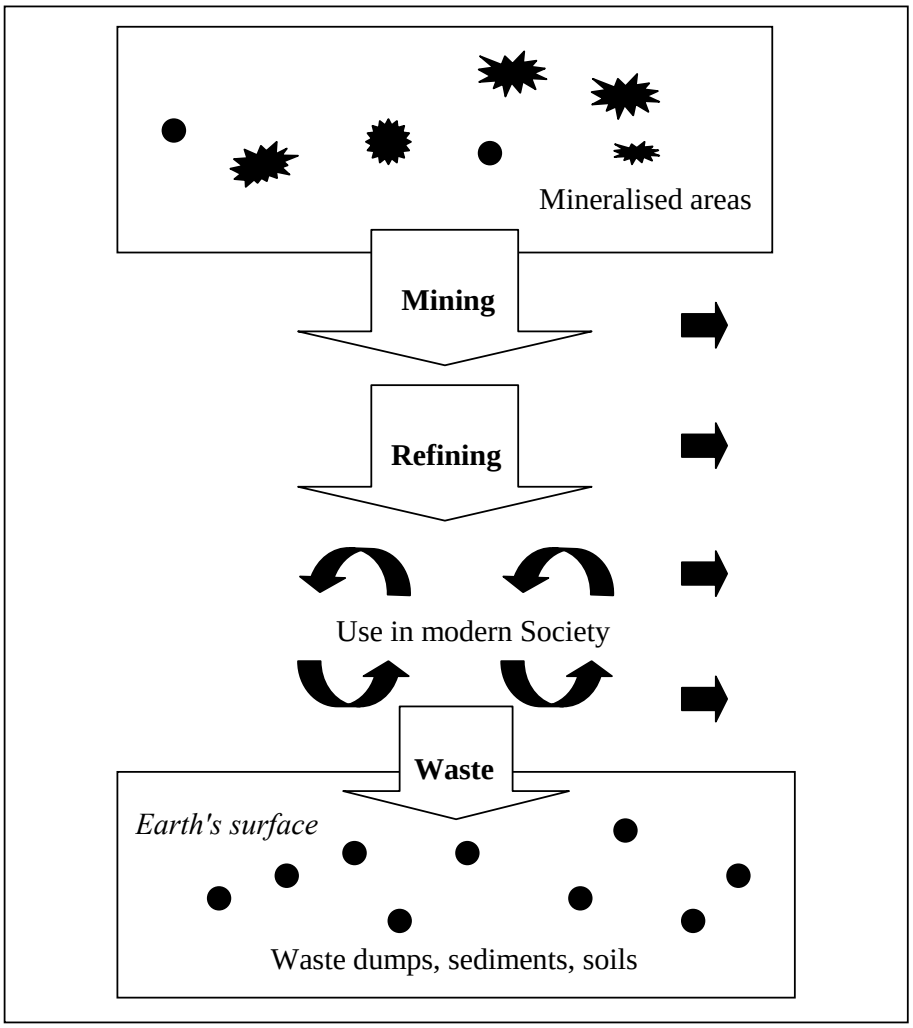

Figure 2.2: Pathway of metals from mineralised areas in the earth's crust to diffuse pollutants in waste dumps, soil and sediments Salomons (1995)

Slanina (1983) suggest that, in order to assess both temporal and spatial changes of a mining environment, sampling is required on a long-term basis, and at large sites. Distance from the mine, wind directions, topography and atmospheric conditions can all have an important influence on the distribution of contamination. Therefore it is often necessary to establish a relatively large number of sampling stations, and to analyse a large number of samples to assess the level of contamination and to delineate areas affected by contamination. Monitoring may involve samples taken close to the mine site as well as far away from the mine site.

$^{206}Pb/^{207}$ Pb ratios and ^{210}Pb Dating

Monitoring of heavy metals in the environment is often facilitated with diagnostic techniques such as the $^{206}Pb/^{207}$ Pb ratio and ^{210}Pb-dating. The isotopic composition of lead ore consist of 4 stable isotopes; the primordial ^{204}Pb and the radiogenic ^{206}Pb, ^{207}Pb and ^{208}Pb. The isotopic ratios $^{206}Pb/^{207}$Pb and $^{208}Pb/^{207}$Pb of different Pb ores varies due to differences in age as well as the U and Th content. Most lead ores in the UK have $^{206}Pb/^{207}$Pb of 1.17 – 1.18 while Tyndrum has $^{206}Pb/^{207}$Pb of 1.144 (Moorbath (1962)). Pb isotope ratios have often been used to characterise sources of contaminant Pb as it is a well-established method. Most studies have acknowledged that the $^{206}Pb/^{207}$Pb ratio is most likely to alter when changes in the environment occurs (Novak et al. (2003)). Previous studies in Scotland have discovered the isotopic signature of $^{206}Pb/^{207}$Pb ratio from various sources as shown in Table 2.3.

Table 2.3: Pb isotope ratio from various sources in Scotland

Pb Source	$^{206}Pb/^{207}$Pb ratio	Reference
Geological bedrock	1.168	MacKenzie and Pulford, 2002
Scottish coals	1.181	Farmer et al. 1999
Leadhills	1.173	Sugden et al. 1993
Tetra alkyl (petrol)	1.09	Sugden et al. 1993

During the 18th and 20th century, atmospherically deposited Pb was derived predominantly from coal burning and processing of indigenous ores. The $^{206}Pb/^{207}$Pb ratios were generally in the range of 1.16-1.17 (Farmer et al. (1999); MacKenzie et al. (1997); MacKenzie et al. (1998b)). However, with the introduction of tetra alkyl Pb, used as an antiknock additive to petrol from the 1920s until 1999, Pb was characterised by an average $^{206}Pb/^{207}$Pb ratio of 1.09 (Sugden et al. (1993)).

As a result, from the 1920s to the late 20th century, a general decrease was observed in the $^{206}Pb/^{207}Pb$ ratio of atmospherically deposited Pb due to the input of petrol derived Pb. The ratios were found to be distinctively in the range of 1.12-1.14 (Farmer et al. (1999); MacKenzie et al. (1997); MacKenzie et al. (1998a)).

The uses of ^{210}Pb-dated cores have also been favoured as a dependable method to characterise historical trends in atmospheric deposition. The use of the ^{210}Pb method as a natural tracer for Pb deposition has been an interest since the early 1960s (Baranov & Vilenskii (1965)). Studies were able to reconstruct historical Pb deposition such as from accumulating ombrothrophic peat deposits from as far back as 300 years as mentioned by Appleby et al. (1988); MacKenzie et al. (1997); MacKenzie et al. (1998b); Shotyk et al. (1996); Shotyk et al. (1997); Shotyk et al. (2002); Weiss et al. (1999).

Lake and river sediment cores have also been proven to be a reliable source for reconstructing past atmospheric deposition of Pb. When applying the technique, it is assumed that the sediments are receiving a constant input of ^{210}Pb from the atmosphere. The ^{210}Pb that was incorporated into the sediments 22.3 years ago will only one half as radioactive as when initially deposited. This logic is extended to calculate the age of sediments at other depths in the sediment column and/or the rate of sediment accumulation (Appleby et al. (1988); Benoit & Rozan (2001); Brenner et al. (2001); Harrison et al. (2003); MacKenzie et al. (1997); MacKenzie et al. (1998b); Turner & Delorme (1996)).

The sedimentation rate in this study is calculated based on the Constant Initial Concentration (CIC). The CIC model assumes a constant initial concentration of unsupported ^{210}Pb and a constant sedimentation rate over a period of time for which the unsupported ^{210}Pb is measurable. The method requires either measurements of sediment porosity to correct for compaction or cumulative dry weight (Turner & Delorme (1996)).

The natural log (ln) of unsupported ^{210}Pb was plotted against the cumulative weight per unit area. The sedimentation rate is derived from the gradient of the plotted graph. The age of the sediment is then obtained by using the formula as follows;

Activity standard:

$$A_t = A_o e^{-\lambda t}$$

$$\lambda = \frac{\ln 2}{t_{1/2}}$$

Where:

A_t = activity after time t

A_o = initial activity

e = natural log the is the Euler number, which is the base of natural logarithms

λ = decay constant

t = time elapsed from Ao

$t_{1/2}$ = half life of 210Pb

$$\text{Sedimentation rate} = \text{- gradient x } \lambda$$

$$\lambda = \text{decay constant}$$

$$= \frac{\ln 2}{t_{1/2}}$$

$$\text{Age} = \frac{\text{cumulative wt/area}}{\text{sedimentation rate}} \text{t}$$

$$\text{Date} = \text{Current year - age}$$

Cochran & Krishnaswami (1980) reports that the use of radionuclides such as ^{210}Pb to date recent sediments is well accepted and established. Another radionuclide, which is often used with ^{210}Pb as an independent marker, is the artificial ^{137}Cs (Benoit & Rozan (2001)). This radioisotope with a half-life of about 30 yr was formed by nuclear fission and has been introduced into the atmosphere since nuclear testing was initiated in early 1950s (Baskaran et al. (1996);Edgington et al. (1991)). Both ^{210}Pb and ^{137}Cs are often used to assist in reconstructing atmospheric fallout as both radionuclides are strongly bound to the sediments and remain in its layers.

As mentioned in Chapter 1, the diagnostic techniques of $^{206}Pb/^{207}$ Pb ratio and ^{210}Pb-dating will be used in this study to facilitate the reconstruction of Pb deposition as well as characterise its source from samples of peat cores and river sediments.

2.2.2 Atmospheric Dispersal and Deposition

Metals introduced into the atmosphere may be deposited on the land surface by precipitation and dry fallout. Additionally, because metals readily adsorb to many sediment types, wind-borne sediment is a potential vehicle for metal transport. Long-range atmospheric transport is one of the main factors for dispersion and deposition of a wide range of pollutants (Steinnes (1997)). The atmospheric dispersal pathway studied in this research focuses on its eventual fallout onto soil and plant surfaces in the vicinity of the mine site. Based on the route of transport of airborne dispersion, the heavy metal's subsequent deposition will provide an insight into the magnitude of airborne contamination. On this basis, tree bark and peat core samples are the focus of this research in providing evidence and information on airborne dispersal of contaminant metals from the mine site.

Heavy metals are taken up to a varying degree by different plants as well as different parts of a plant species (Saarela et al. (2005)). Mosses, lichens and trees are often used to provide data for atmospheric deposition, not only for the current contamination condition but also for the reconstruction of historical records as mentioned by Farmer et al. (2002); Poikolainen et al. (2004); Zhang et al. (2002). An example of this was the use of archived samples of Scottish *Sphagnum* mosses that were used to recreate a historical record of lead deposition in Scotland (Farmer et al. (2002)). The study was made to test the validity of historical records that were derived from lake sediment and peat bog profiles. The mosses were used to investigate the inputs made by different, isotopically distinguishable sources of the atmospheric Pb burden. This was made possible as the mosses were taken from the Herbarium Collection at the Royal Botanic Garden, Edinburgh, which had moss samples collected over a span of 160 years.

As shown in Figure 2.3, the decline of $^{206}Pb/^{207}Pb$ ratio from the 1930s until 1980s was due to the growing influence of car-exhaust emissions of Pb from the use of alkyl lead additives in petrol, $^{206}Pb/^{207}Pb$ ratio (1.06-1.09), which was also dominated by the use of Australian lead (1.04). The trend also corresponded to the lake sediment and peat bog records.

After the 1980s however, the increase in the $^{206}Pb/^{207}Pb$ ratio reflects the reduction of the maximum permitted lead concentration of leaded petrol. It also shows the impact of unleaded petrol in the UK and its subsequent ban of leaded petrol in early 2000. The overall study was able to show reduced lead emissions over the past 20 years in the U.K. based on the Scottish Sphagnum moss.

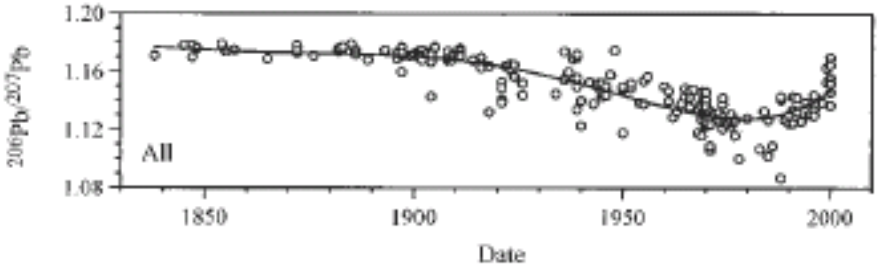

Figure 2.3: Individual $^{206}Pb/^{207}Pb$ ratios for 198 Scottish Sphagnum moss samples against year 1838-2000 (Farmer et al. (2002)).

Deposition on to tree bark

The annual rings of trees from temperate regions have been used to investigate the chronological records of trace element pollution in the atmosphere. Known as dendroanalysis, this method is based on the assumption that the stability of mineral distribution patterns and elemental concentrations in individual tree rings are not subject to any radial movement within the tree. Amato (1988) suggests that the chemical composition of individual tree rings may disclose the chemical composition of the environment at their time of its formation. In southern Norway, Aberg et al. (2004) showed good correlation of Pb isotope data from peat cores with tree rings and bark pockets from pine trees.

Baes III & McLaughlin (1984) observed that multi element analysis of tree rings from short-leaf pine trees was able to provide information on temporal changes in air pollution and acid deposition. Their study found a correlation between an increase in iron concentrations in tree rings corresponding to periods with a regional increase in fossil fuel combustion and smelting activities.

However, some historical studies using tree rings were not as successful and have raised doubts on whether the relative concentration of the trace elements accurately reflects relative changes in the environment. Nabais et al. (1999) reported several weak aspects of dendroanalysis such as the influence of seasonal variations on the concentration and distribution pattern of elements. Figure 2.4 shows the *Fagus sylvatica* tree displaying different levels of Pb throughout the season, with higher concentration during dormant and budding months (December and April) while lower concentrations were observed during spring and summer (Hagemeyer & Schafer (1995)). The study suggests that the xylem sap or sapwood, which carries water and mineral nutrients, is responsible for the seasonal fluctuations due to variations in the quality and composition of the sap through the year. For instance, higher velocities of transpiration stream in spring increases the rate of exhaustion of mobile elements in stem wood that are not rapidly replaced by root uptake.

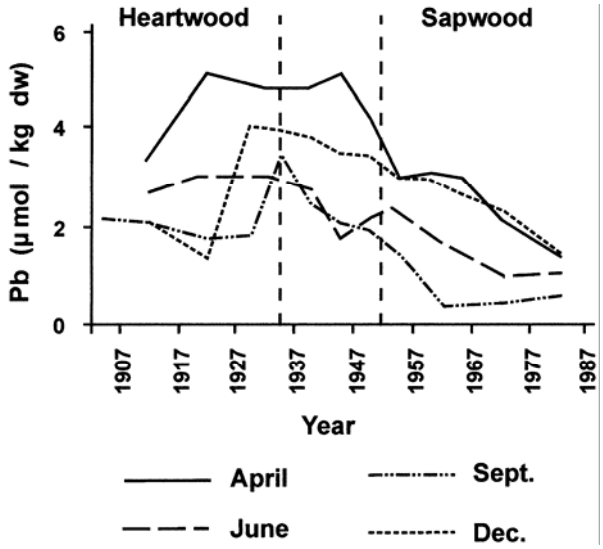

Figure 2.4: Seasonal variations in concentrations and radial distribution patterns of Pb in wood (Hagemeyer & Schafer (1995)

Hagemeyer & Schafer (1995) also observed mobile peaks of Cd at the boundaries of sapwood-heartwood of *Quercus robur* trees.

Figure **2.5** shows a cross section of a tree bark containing different tissue layers, which includes the sapwood and heartwood. The study found that peaks in Cd concentration did not agree with the occurrence of pollution events in the environment of the trees, as shown in Figure 2.6. This suggests that the radial distribution of Cd in the tree stems is influenced by the location of the border between the sapwood and heartwood. Brackhage et al. (1996) also reported inconsistency in patterns of elemental concentrations observed in stem wood of trees with known pollution inputs. The tree ring record of Scots pine trees, which were grown on experimental plots containing heavy metals, did not accurately respond to the time of the pollution event that took place 12 years earlier. Other studies have also indicated reservations and concerns on the use of dendroanalysis due to the radial mobility of elements within the cells (Bellis et al. (2001b); Watmough (1999)).

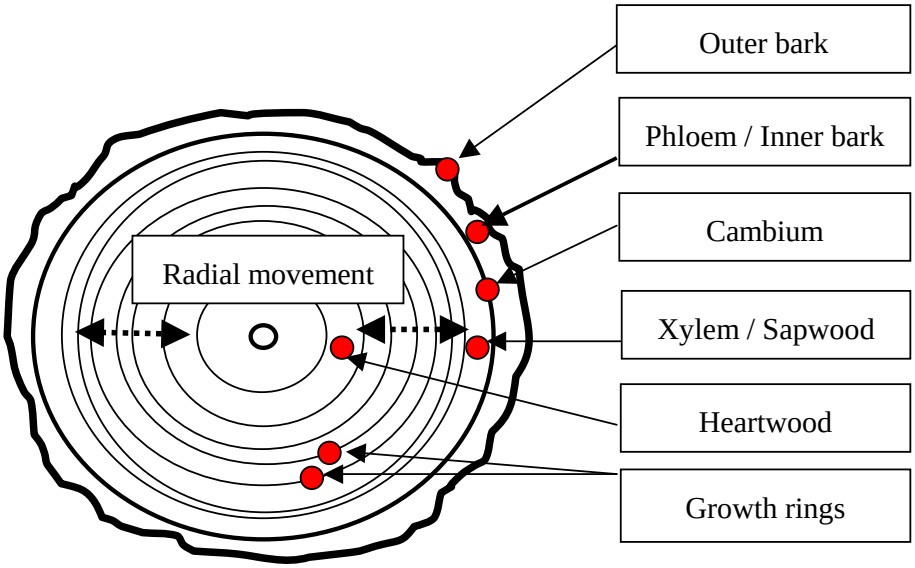

Figure 2.5: A cross sectional diagram of a tree trunk illustrating the different layers and radial movement (↔) of elements between cell layers.

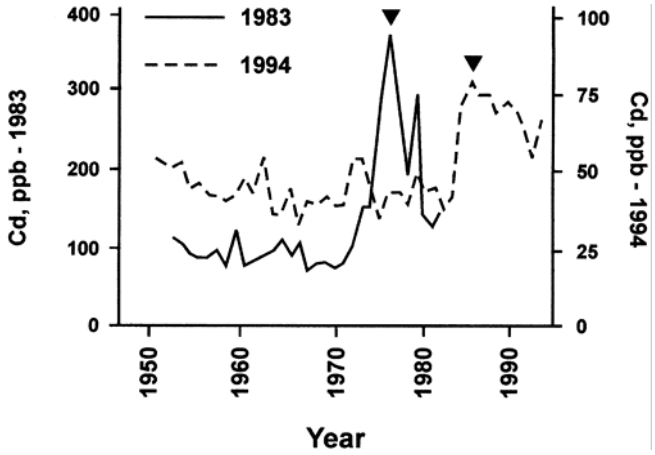

Figure 2.6: Radial distribution of Cd in stem wood indicating transition between sapwood and heartwood at the time of sampling (Hagemeyer & Schafer (1995)).

Tree bark pockets have also been used as an archival indicator of heavy metal pollution. This unique feature in trees is formed by the enclosure of surface bark by the trunk during growth and is subsequently dated using annual growth rings (Tye et al. (2006)). Hence, the bark pockets are isolated from further atmospheric input and can act as an excellent "time capsule" retaining information about the environment at their time of formation as mentioned by Bellis et al. (2002). In Japan, Satake et al. (1996) collected evidence of atmospheric dispersal using tree bark pockets and compared it against records taken from the outer bark of a tree containing lead deposition from a total period of 40 years. Evidence of an increase in lead pollution due to the use of leaded gasoline in Japan was successfully re-created, proving the validity of bark and bark pockets as reliable pollution indicators. One of the drawbacks of this method however, is that it relies on the availability of felled or fallen trees containing suitable bark pockets.

In view of the objectives of this study, tree bark was selected for use as an indicator of contamination levels related to atmospheric dispersal of heavy metals from the study site. Tree bark is widely used as it provides a cheap and simple tool for monitoring trace metal levels in the atmosphere.

The bark surface is porous and the absence of metabolic processes makes it almost inert in the presence of inorganic and organic substances. It also shows good accumulation properties in relatively short times (Schulz et al. (1999)). Tree bark has been shown to be able to indicate levels of airborne pollutants such as Pb, Zn, Cu, Cr, Ni, Cd, Mn, Fe, U, Pt, as reported by Bellis et al. (2001a); El Hasan et al. (2002); Odukoya et al. (2000); Saarela et al. (2005); Turkan et al. (1995). The use of tree bark as a monitoring tool ensures the survival of the tree itself as reported by Odukoya et al. (2000). Unlike in the use of tree bark pockets, tree bark is collected without felling or permanent disfigurement of the tree, enabling continuous monitoring over a considerable period of time throughout the life of the tree.

Although tree bark has been shown to accumulate airborne particles, it may not be a suitable sampling matrix for reconstruction of historical trends in atmospheric deposition as bark is subjected to regular shedding. This normal development of trees is caused when continued growth pushes the bark outwards, causing the outer layers to crack and fall off (Borger (1973); Esau (1965)). The bark that is shed is known as the ‘outer bark’, which consists of dead tissues. This is replaced by ‘inner bark’, which consists of the phloem and the living tissues of the inner periderm (Eames (1947); Esau (1965); Srivastava (1964); Srivastava (1966)). In pine bark, the external sheet is shed after about 2 years and new layers of 1-2 mm thickness are formed from inside (Schulz et al. (1999)). This means that the timescale for contaminant deposition recorded on bark surfaces is subject to the bark’s regeneration time.

Schulz (Schulz et al. (1999); Schulz & Schulz (2000)) observed contaminant accumulation on the surface of a piece of pine bark using laser ablation ICP-MS. As shown in Figure 2.7, the distribution of three elements; sulphur, iron and calcium indicated that accumulation takes place on the outer, porous layer of the bark surface. A significant concentration gradient is observed between 0.5 and 1.5 mm depth in the bark, with lower concentrations in deeper layers. Thus, collection of the outer 2 mm of bark will be sufficient to show atmospheric deposition.

Schulz also explains in his study that the atmospheric deposition processes to which pine bark is subject, involve both wet and dry deposition. Figure 2.8 illustrates that bark deposition involves crown throughfall, dry deposition and stemflow.

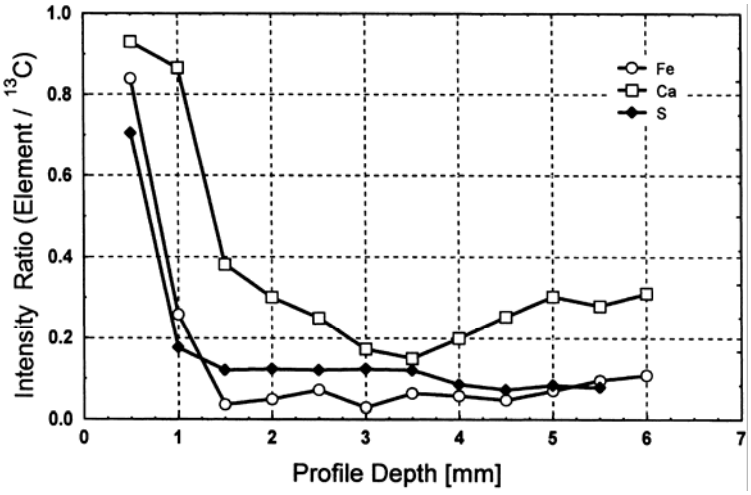

Figure 2.7: Bark profile analysis that was performed with a Laser ICP-MS. The intensities were measured in 0.5 mm steps (Schulz et al. 1999)

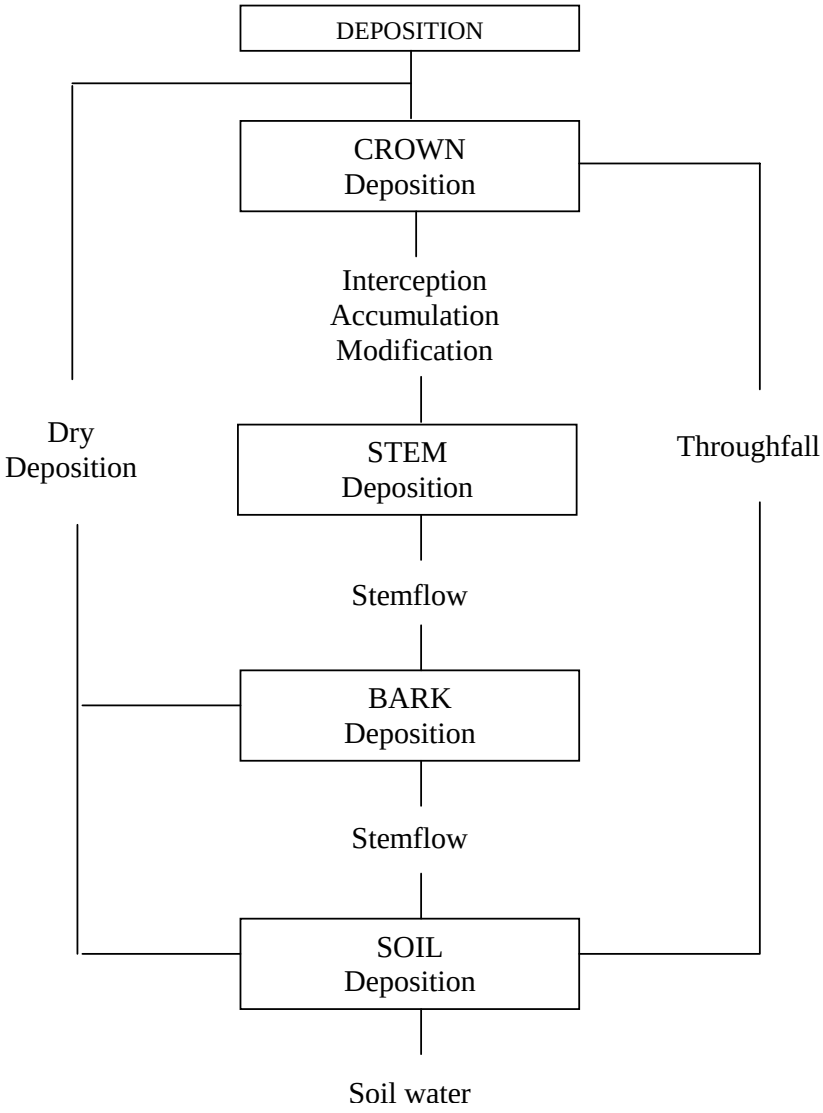

Figure 2.8: Accumulation processes in pine bark (Schulz et al. 1999)

Table 2.4 summarises data from various studies on Pb levels in tree bark from diverse types of tree species and locations. Tree bark samples containing high concentration of Pb were derived from locations, which were affected by specific sources of contamination such as smelters or traffic, in contrast to remote areas where lower concentrations were observed.

Table 2.4: Pb concentrations in Tree Bark from various studies

Location	Tree Species	Pb ($kg\ m^{-1}$)	Reference
North Ferriby, Humberside Smelter, UK	*Fagus sylvatica*	2100	Tye et al. (2006)
Urban Forest, Greece	*Pinus halepensis*	15	Michopoulos et al. (2005)
Industrial Area, Jordan	*Cyprus semervirens*	290	El Hasan et al. (2002)
Scilly Isle (Rural), UK	*Fagus sylvatica*	10	Bellis et al. (2001a)
Derby Power Station, UK	*Fagus sylvatica*	287	Bellis et al. (2001a)
Darley Lead Smelter, UK	*Fagus sylvatica*	9600	Bellis et al. (2001a)
High Traffic Area, Nigeria	*Azadirachta indica*	73	Odukoya et al. (2000)
Background Level, Norway	*Pinus sylvestris*	2	Schulz et al. (1999)
Industrial Area, Germany	*Pinus sylvestris*	21	Schulz et al. (1999); Schulz & Schulz (2000)
Rural Area, Poland	*Pinus sylvestris*	5	Schulz et al. (1999)

The investigation of atmospheric dispersal in this study will incorporate the use of tree bark as the area of study has a forest stand that is accessible. Apart from that, peat samples will also be used as indicators of atmospheric dispersal based on the eventual fallout of airborne particles. Core samples of peat will also be able to provide information on the historical atmospheric condition based on the deposition accumulated within its layers.

Deposition on peat

Peat has been widely used in monitoring heavy metal contamination where historical trends can be reconstructed based on the depositional fluxes of contaminants within the profile. Peat contains mostly diamagnetic organic matter, which is an excellent accumulator of all kinds of atmospheric dusts and industrial pollution (Strzyszcz & Magiera (2001)). Peat studies have found to be consistent with data derived from lake sediments as well as archived herbage samples as reported by Bacon & Hewitt (2005); Brannvall et al. (1997); Farmer et al. (1997b); Farmer et al. (2002); MacKenzie et al. (1998a); Sugden et al. (1993).

Peat contains mostly organic matter produced by partial decomposition of plants, mosses and trees. Generally, peat is formed under the condition of poor drainage and is a natural precursor of coal. When dried, peat can be used as organic fuel for domestic heating or even power generating stations due to its high organic content. Major peat users include countries such as Finland, Ireland, Russia and Sweden. There are various types of peat from diverse peatlands worldwide, referred to according to its location and source, such as the forest-type peat, moor peat, *Sphagnum* peat and the ombrotrophic peat[5]. Ombrotrophic peat bogs have great potential to offer records for atmospheric deposition of immobile heavy metals such as Pb and provide no measurable chemical influence by groundwater (Shotyk et al. (1996)).

Weiss et al. (1999) reported that past atmospheric Pb deposition in Switzerland was mainly studied using lake sediments although it is subjected to critical limitations as lake sediments are influenced by lithogenic inputs from catchment soils and rocks. The study suggests the use of ombrotrophic peat bogs as an alternative, as they are influenced solely by atmospheric input and receive water and nutrients by dry and wet deposition. Nevertheless, Weiss states that if ombrotrophic peats are utilized as archives, it is essential to carry out geochemical studies to confirm that the samples are purely ombrotrophic.

Using the ^{210}Pb-dating technique, the age of the peat profile could be estimated and together with the dry weight and age of the core at different depths, the accumulation rate (mg m^{-2} y^{-1}) could be calculated (Jensen (1997)).

Kylander et al. (2005) used an 8000 year-old peat core from the SW of Spain to trace detailed sources of both natural and anthropogenic Pb. The study found an average net Pb accumulation rate of 0.032 mg m^{-2} y^{-1}, which is 2.5 and 3 times higher than those found in Switzerland and Sweden, respectively. The ^{206}Pb/^{207}Pb signature of 1.24 was also recorded which is comparatively more radiogenic and characterised significant Pb contamination contributed by past mining activities in Spain. The study also supports the use of Pb isotopes as reliable environmental substitute in peat studies although stresses the importance of performing regional studies of atmospheric dust and heavy metal deposition to understand past and present deposition.

Generally, applying the Pb isotope technique assumes the immobility of Pb within the peat, an assumption that has been frequently challenged. Vile et al. (1999) found that soluble Pb was retained in peat due to the binding of Pb^{2+} with organic matter in peat. This finding gives credibility to the ^{210}Pb-dating method using peat with high organic content such as the *Sphagnum* peat deposits. A study by Cloy et al. (2005) using ombrotrophic peat also reveals immobility of Pb within its peat profile. Figure 2.9 shows a Pb concentration profile of a Flanders Moss peat core from Central Scotland, corresponding to the dates derived from the ^{210}Pb method.

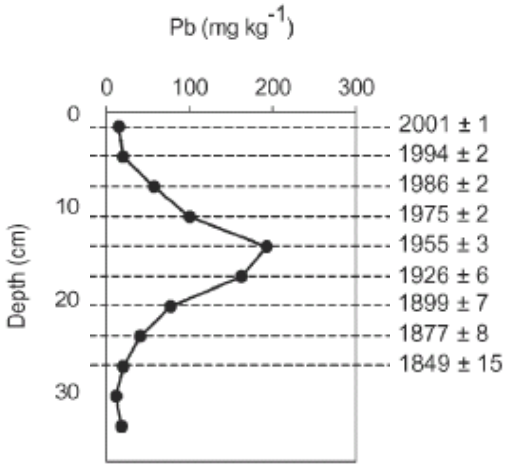

Figure 2.9: Pb concentration (mg kg^{-1}) profile in a ^{210}Pb-dated Flanders Moss core (Cloy et al. 2005)

The work by Cloy et al. (2005) also found a maximum of ~ 21 mg m^{-2} y^{-1} of anthropogenic Pb flux during the period 1920s to 1950s and its subsequent decline towards the end of the 20th century (Figure 2.10). The study suggests that the trend reveals the influence of coal combustion emissions. The ^{206}Pb/^{207}Pb ratio meanwhile shows a reduction caused by the use of alkyl lead additives in petrol. The rise during the beginning of the 1980s reflects the phasing out of the leaded petrol and the introduction of unleaded petrol. The trend of the ^{206}Pb/^{207}Pb ratio shows good agreement to the Scottish *Sphagnum* moss previously discussed (Figure 2.3).

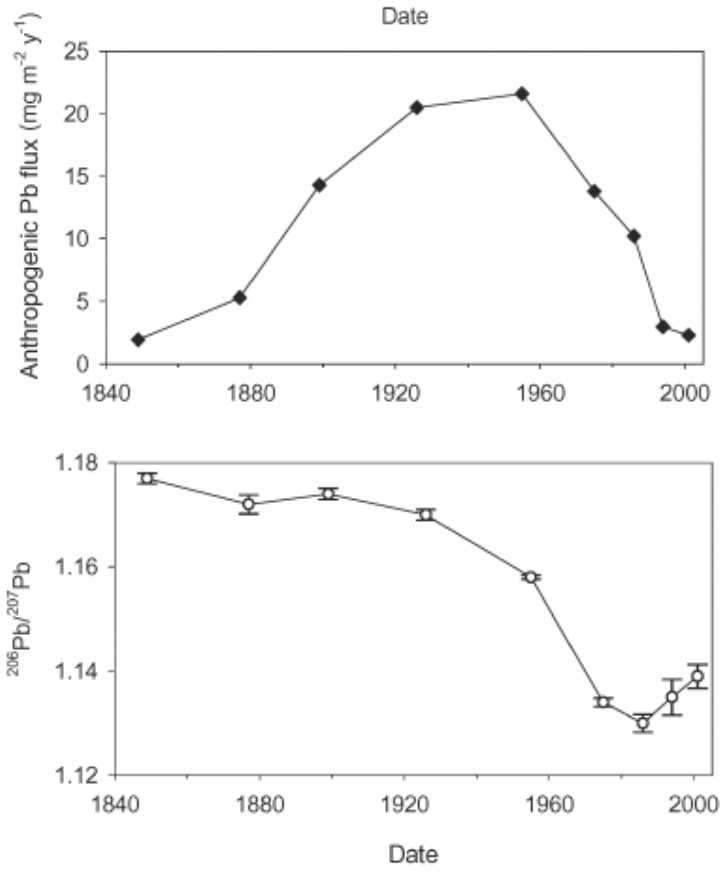

Figure 2.10: Anthropogenic Pb flux (top) and $^{206}Pb/^{207}Pb$ ratio from Flanders Moss, Scotland (Farmer et al. 2005)

2.2.3 Fluvial Dispersal and Deposition

Fluvial dispersal has been an important pollution pathway in the United Kingdom in areas of metal mining since the nineteenth century. Before pollution controls were introduced in 1876 (Harrison (2001)), Pb-Zn mines discharged waters from ore dressing operations directly into streams and rivers. This led to the alluvial soils in most flood plains of rivers draining mining areas being severely contaminated with Pb, Zn and other metals (Merrington & Alloway (1994a); Merrington & Alloway (1994b)). Metals that are released into the atmosphere due to extraction and processing activities can enter the hydrological cycle, either during use or as a result of their subsequent disposal (Foster & Charlesworth (1996)).

Hudson-Edwards et al. (1996) conducted mineralogical analysis of riverbank and riverbed sediments, mine-waste tips and suspended solids in river water. Evidence of historic mining was found to be the cause of widespread Pb, Zn, Cd, and Cu contamination in the fluvial deposits of the Tyne River Basin, northeast England. In the River Severn, Wales, vertical alluvial profiles were found to be contaminated with heavy metals following extensive metal mining in the upper catchments area during the mid-19th century (Taylor (1996)).

In Scotland, the effects of past mining in fluvial system such as lake and river sediments have been the subject of various studies into historical elemental deposition by researchers (Eades et al. (2002); Farmer et al. (1980); MacKenzie & Pulford (2002); Patrick & Farmer (2007); Rowan et al. (1995)). As previously mentioned in Chapter 1, Farmer et al. (1997a) found inconsistently high levels of Pb in sediments from Loch Tay, central Scotland, and suggested that the contaminant Pb originated from the mining activities in Tyndrum. The claim was made on the basis of the consistent $^{206}Pb/^{207}Pb$ ratio found in the Loch Tay sediments with Tyndrum ore deposits of 1.144 (Moorbath (1962)) and the Pb deposition that corresponded to the time of mining and processing at Tyndrum. Figure 2.11 shows the fluxes and $^{206}Pb/^{207}Pb$ of excess Pb found in the sediments based on the ^{210}Pb-derived sedimentation rate of 28.3 mg m^{-2} y^{-2}.

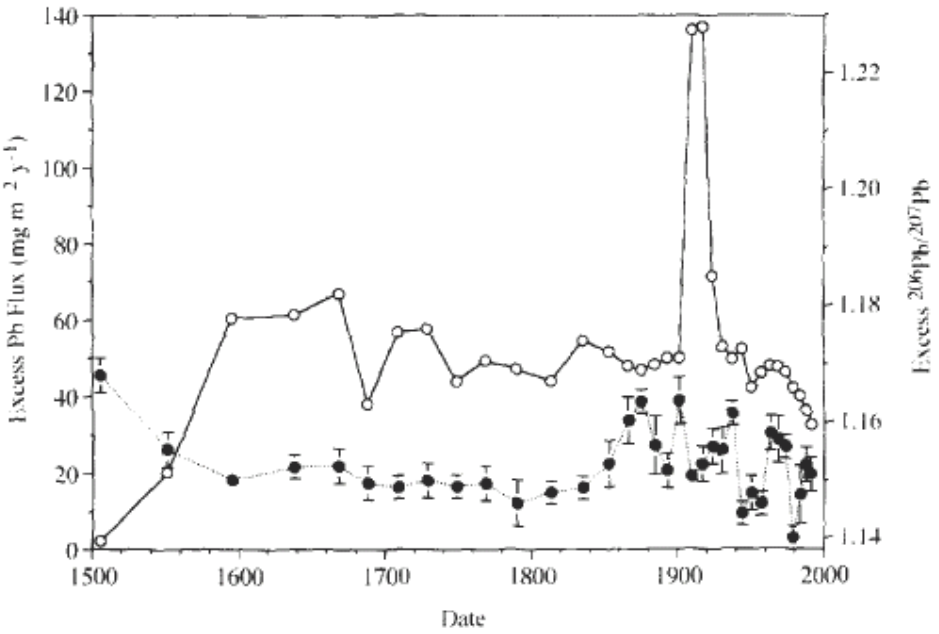

Figure 2.11: Fluxes (open circles) and $^{206}Pb/^{207}Pb$ (closed circles) of excess Pb deposited in the sediments of Loch Tay (Farmer 1997a)

However, given the relatively large distance (approximately 25km) between Loch Tay and Tyndrum, and the presence of several lakes (which act as sediment traps) along the watercourse, further evidence was required to confirm the suggested fluvial transport. The current study thus includes investigation of fluvial dispersal beginning from the outflow from Tyndrum extending 25km towards Loch Tay.

Rowan et al. (1995) conducted a study on the Glengonnar Water, Scotland which is situated near the mining districts of Leadhills and Wanlockhead and found approximately 15 000 mg kg^{-1} and 33 000 mg kg^{-1} mean concentration of Pb from channel sediments and floodplain soils respectively. The mining districts once supplied more than 90% of total Scottish production and 10% of national UK output of lead. The past legacy has now contributed to Pb concentration 30 times higher than the current action trigger level for grazing livestock on reclaimed mining land. The study by Rowan et al. (1995) presents an example of heavy metal dispersal through fluvial system supplied from the former mine site.

Dispersal of heavy metals via fluvial transport has also been reported in other parts of the world, with resultant contaminants threatening crops as well as human health. In the northwest of Korea, a Pb-Zn mine has been identified as the source of high concentrations of Cd, Cu, Pb and Zn in paddy soils, rice plants and irrigation waters due to the seepage of metals from mining dump sites. The average daily intake from locally grown rice by residents nearby was estimated to be 121μg Cd and 126 μg Pb (Jung & Thornton (1997)). This markedly exceeds the guidelines of intake recommended by the FAO and the WHO.

In Malaysia, Ang & Ho (1994) reported high levels of As, Pb and Hg in ground and surface water of idle tin tailings at the former tin mine town in Bidor. Potential Toxic Elements (PTEs) found in crops grown on former mine land and irrigated from mining ponds were also found to have exceeded the permissible limits as stipulated by the Department of Environment (DOE) of Malaysia.

Examples of heavy metal deposition in sediments are shown in Table 2.5, which displays Pb concentration data collected from Scotland and Greenland from various areas representing marine and freshwater sediments. Maarmorilik is a former Pb and Zn mine known as The Black Angel, which operated between 1973-1990, while Affarlikassaa represents natural deposits of Pb and Zn. The study conducted by Larsen et al. (2001) reveals highly elevated Pb concentration of almost 350 times in sediments from the former mine site compared to the remote site in Affarlikassaa.

The Minch, a remote area in the North of Scotland, reveals very low Pb concentration that differs greatly from locations such as former mine sites, as well as industrialized and populated areas such as the Clyde estuary. The Pb concentration from the lake of Lochnagar (Yang et al. (2002)) on the other hand, which displays deposition solely on atmospheric fallout still reveals the presence of Pb deposition within the water system through atmospheric deposition even though no distinguishable inflow enters the lake.

Table 2.5: Pb concentration in sediments from various backgrounds

Description	Location	Pb (μg g-1 dry weight)	Reference
Former Pb/Zn mine	Maarmorilik, West Greenland	89220a	Larsen et al., (2001)
Uncontaminated site	Affarlikassaa, West Greenland	250a	Larsen et al., (2001)
Former Pb mine	Leadhills, Scotland	15300a	Rowan et al. (1995)
Industrialized and populated area	Clyde Sea Area, Scotland	5200a	Farmer J. G., (1982)
Remote site	The Minch, Scotland	10.6a	Farmer J. G., (1982)
Catchment lake	Lochnagar, Scotland	100-360[b]	Yang et al., (2001)

Note: a-maximum concentration from core samples
b-concentration from bulk samples

In order to understand and evaluate the extent of mining activities on the fluvial environment, investigation into all aspects of the fluvial system is required. Miller (1997) stressed that fluvial geomorphic processes are of fundamental importance in the transport and fate of heavy metals derived from mine sites. The fate of metals within mine sites tends to be more complex than from other sources because of temporal and spatial changes in the types, rates, and magnitudes of erosion and depositional processes. This leads to greater environmental consequences because greater quantities of contaminated debris are stored along the channel margins where it can be eroded and sporadically redistributed during times of flood.

It is not uncommon for more than 90% of the total metal load in rivers to be transported in the solid phase, either adsorbed onto particle surfaces and coatings, or incorporated into mineral grains. Kennish (1992) reports that heavy metals can exist in surface waters in colloidal, particulate, and dissolved phases, although dissolved

concentrations are generally low. The colloidal and particulate metal may be found adsorbed to clay, silica, or organic matter. The soluble forms are generally ions or unionized organometallic complexes.

In lakes and reservoirs, significant reductions in velocity at the point of inflow, and the large water storage capacity relative to inflow, will result in the deposition of coarse sediments in deltas and fine sediments in the deep-water regions, a process known as focusing (Foster & Charlesworth (1994)). These fine sediments may contain high heavy metal concentrations simply as a function of sorting and enrichment relative to catchment source materials (Peart & Walling (1982);Novotny (2002)). Yang et al. (2002) mentions the events of sediment focussing processes in lake sediments as the occurrence of waves and water currents which re-suspend sediments in shallow areas, transports and settle sediments at deeper areas.

In a river system, downstream reductions in contamination due to metal dispersal and dilution are often observed and modelled, particularly those associated with mineral extraction activities from point source inputs (Bradley & Cox (1986); Macklin (1985); Wolfenden & Lewin (1977)). Rowan et al. (1995) reported that floodplain sediments (riverbank) have the potential to be used for reconstructing histories of flooding. The study carried out at the River Tay, Scotland showed that low-frequency, high-magnitude flood records are preserved while sedimentary records of frequent overbank spills are not.

Buffle & Leppard (1995) gave an explanation of the characteristics of aquatic colloids and macromolecules to better understand their role as carriers of trace compounds. In surface waters, colloids (1 nm to 1μm in size) create unstable suspensions in aquatic system, as they tend to go through conformational changes, aggregate, and then sediment. Due to their small size, they are not able to settle on their own except if they coagulate and form aggregates large enough to sediment. Figure 2.12 illustrates the process of coagulation and sedimentation of colloids within the fluvial system.

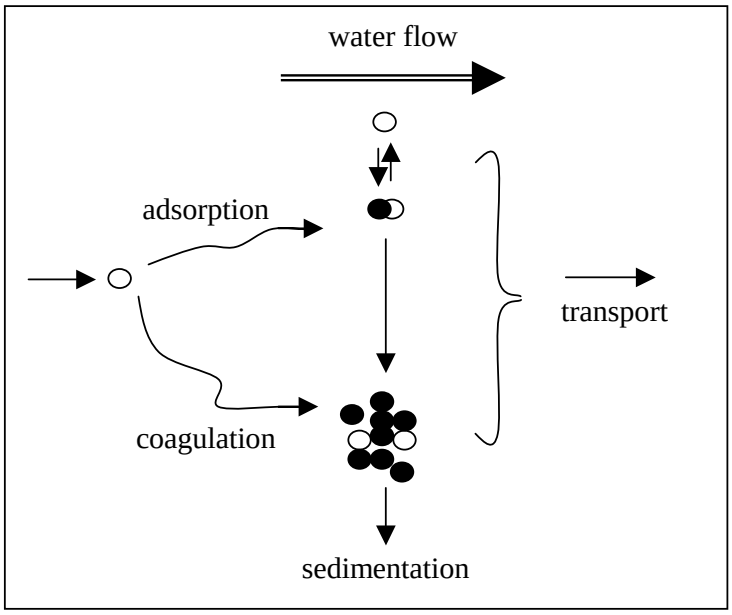

Figure 2.12: Schematic representation of the transport of vital and toxic compounds (lighter circles) and colloidal carriers (darker circles) in surface waters (Buffle & Leppard 1995).

An understanding of the contribution made by the sediment-associated fraction to the total load requires knowledge of the effects of particle size, organic matter content, sediment surface area and the surface coatings on the suspended particles. Robinson & Slingerland (1998) demonstrated that a negative correlation exists between sediment size and metal concentrations. Particle size is one of the most important physical controls when relating conditions of heavy metals that are carried by suspended sediment.

In the present study, the concentration of heavy metals within suspended particles and riverbed sediments was analyzed based on different size particles to investigate the association between heavy metal concentrations and size fraction. The magnitude of fluvial dispersal of heavy metals from the former mine will include investigation of the solution phase, suspended particles, riverbed and riverbank cores. This includes the characterization and historic reconstruction of heavy metal deposition using stable Pb isotope ratios and ^{210}Pb-dating methods.

CHAPTER THREE

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3.0 SAMPLING SITE AND METHODS

This chapter describes the sampling site, sampling procedures and the analytical methods applied in this research. It is divided into three sections. The first section describes in detail the features of the sampling site. This consists of two areas: the main area of the ex-mine site in Tyndrum and an area covering 25 km of the river system downstream from Tyndrum.

The following section of this chapter explains the sampling techniques applied on site while the final section explains the methodology of the laboratory analyses that were involved in this research. All results from the analyses are presented and discussed in the following chapter.

3.1 Sampling Site Description

This section explains the details and features of the sites where samples were collected. The first focus is on the area of the former mine site at Tyndrum and the second area covers the outflow of the river system downstream from Tyndrum. Maps, photos and figures are used to provide clearer descriptions of the sampling locations.

3.1.1 Tyndrum Main Site

The former mine site at Tyndrum (OS NN 331 303) is located on a hillside at a height of some 600 m, approximately 1 km to the west of the village. The overall area of the main mine site is as depicted in the Ordnance Survey UK 2005 (OS) map in Figure 3.1. The main mine site also has the remains of what appear to be the station/ track, which was used for transporting ores from the main lead veins, and which end at the foot of the hill. This was the location where the ore processing was believed to have taken place and where the waste was eventually dumped.

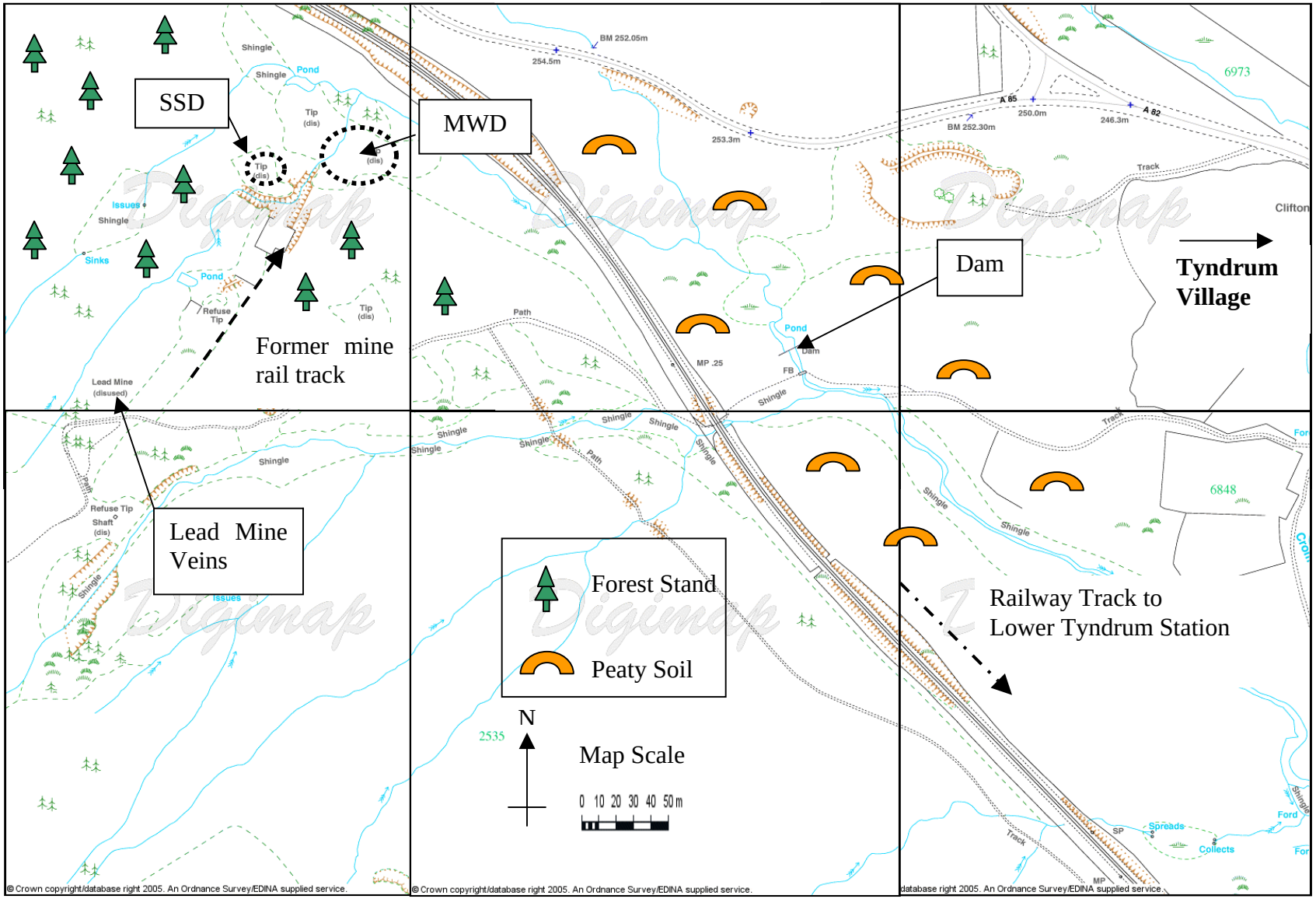

Figure 3.1: Ordnance Survey UK 2005 (OS) Map of the Tyndrum Main Site

The two dumpsites are identified in this research as the Main Waste Dump (MWD) and the Small Side Dump (SSD). At present, both are obvious visible features that reflect the workings of the mine. This can be clearly seen in a photo of the site in Figure 3.2. The dumpsites are noticeable even from afar, because these areas have little or no vegetation unlike the wooded area surrounding them.

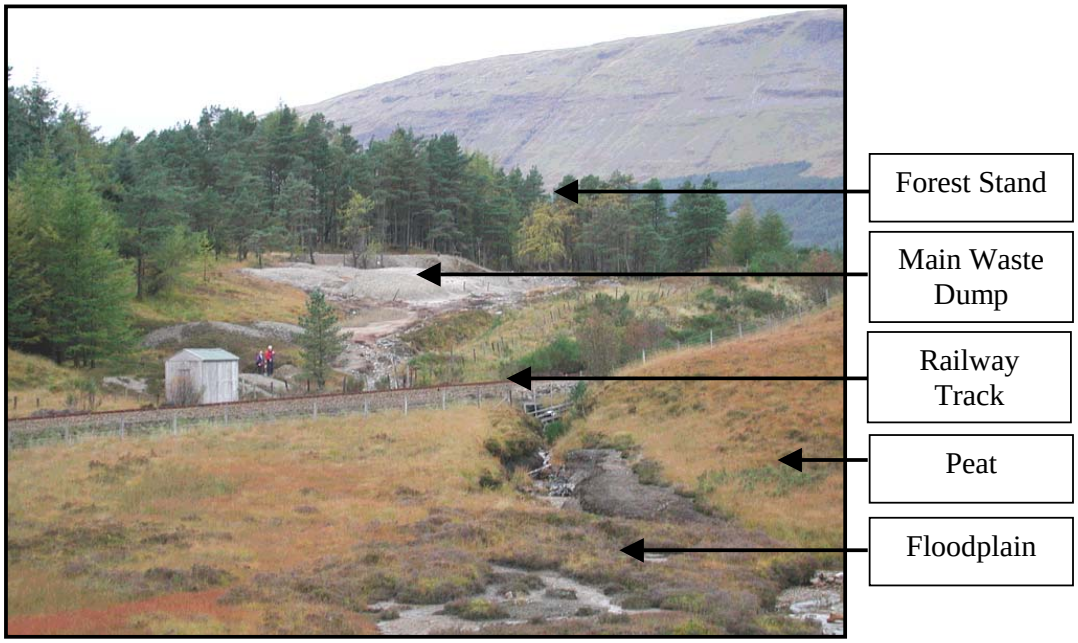

Figure 3.2: Tyndrum Former Mining Site

The Main Waste Dump (MWD), which covers an area of approximately 300 m^2, contains loose sandy waste and is devoid of any living vegetation as clearly shown in the photo in Figure 3.3. The waste is also dominated by coarse material, with 73.2% being greater than 180 µm and only 3.8% less than 53 µm. The smallest size fraction was found to contain approximately 4.5 % of Pb and 0.97 % of Zn (MacKenzie & Pulford (2002)). The Small Side Dump (SSD), on the other hand, supports a sparse but reasonable surface layer of vegetation, mainly grasses, moss, small shrubs and small tree seedlings. This dump covers a smaller area of about 100 m^2. Unlike the MWD, the SSD has yet to have records on its characteristics as well as measurements of Pb and Zn concentration in its core profile.

Figure 3.3: Main Waste Dump (MWD)

Since mining ceased in the 1920s the mine site has been left derelict and the former mine area contains only the ruins of the original buildings and other workings. The thick forest stand that can be seen within the area is partly the result of plantation efforts by the Forestry Commission of Scotland. This may perhaps be the only recorded activity within this area after mining had stopped. Figure 3.4 shows a Stock Map of Tyndrum provided by the Forestry Commission. It depicts the different areas where the trees were planted according to species and planting year. This dates back to as far as 1891 and as recent as 1990.

The trees within this area include species that are native to Scotland or hybrids from other parts of the continent. Amongst them are the Scots Pine (*Pinus sylvestris L*) - SP, Sitka spruce (*Picea sitchensis*) - SS, European Larch (*Larix decidua*) - EL, Japanese Larch (*Larix kaempferi)* - JL, Lodgepole Pine (*Pinus contorta)* - LP, Norway spruce *(Picea abies)* -NS and mixed broadleaf species – MB. The forest stand covers a wide area of the hillside in Tyndrum, mainly towards the west and south of the railway track. This area provided a suitable resource for the purpose of collecting bark samples for this study.

The surrounding area is covered by peaty soil especially in the open area on the east side of the rail tracks. The OS map in Figure 3.1 shows the main peat-covered areas. There is also no forest plantation within this area as clearly shown in the Tyndrum Stock Map (Figure 3.4). This area is situated between the former mining area and the residential area of Tyndrum, where the main river draining the Tyndrum valley passes through. Several profiles of peat cores were collected within this area for the study.

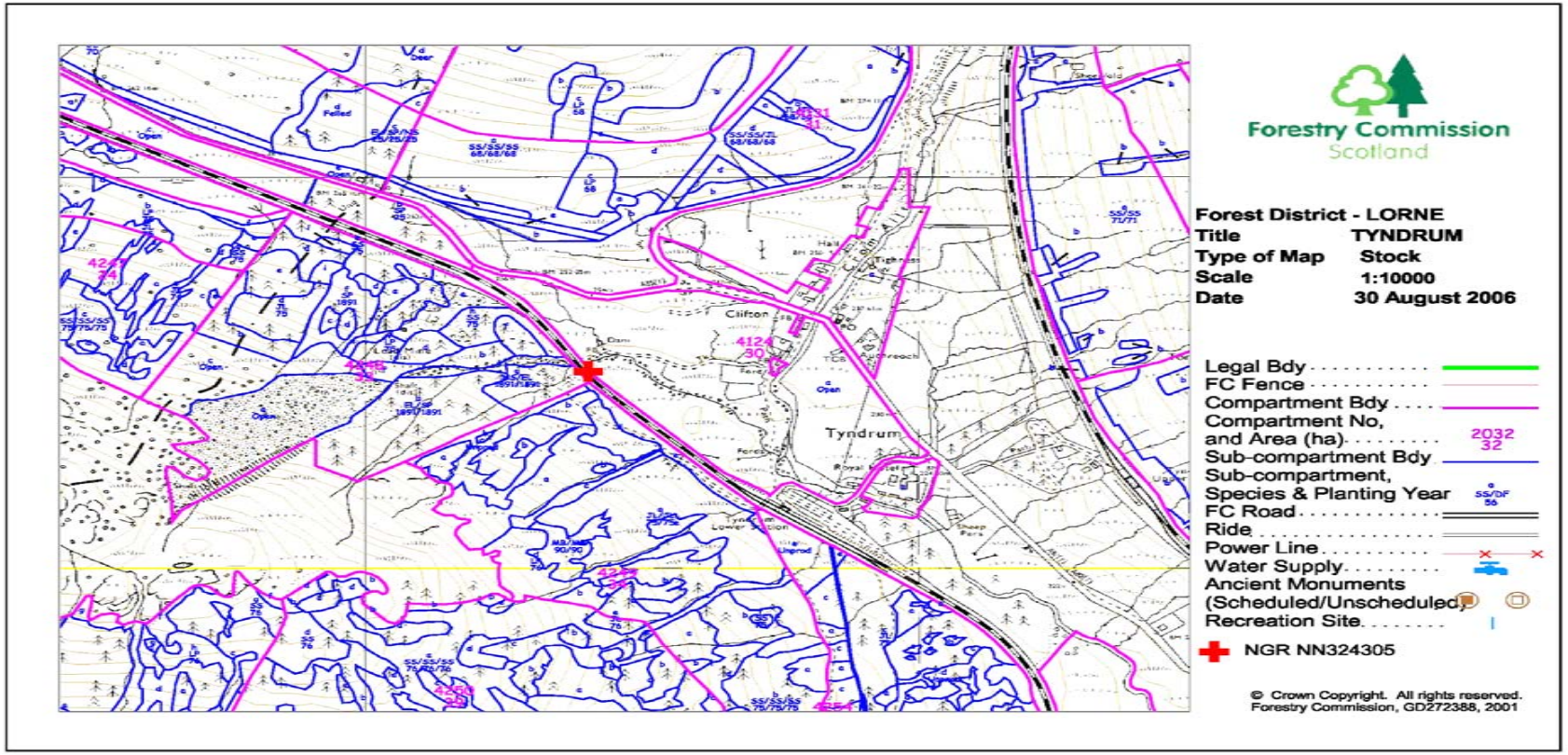

Figure 3.4: Tyndrum Stock Map (Forestry Commission Scotland)

The main mine site also has a network of streams that run through the area from the Tyndrum hillside. There are two main streams that flow into the mining area as illustrated in the OS map. The streams are approximately 1-3 meter wide and 0.5-1 meter in depth. Apart from this, there are several other smaller streams, which run within the area, which are not identified in the OS map but are illustrated in the sampling map in Figure 3.11. The smaller streams are approximately 0.5-1 meter wide and about 0.5 meter deep. Most of the banks of these streams show evidence of metal contamination, as there is no vegetation within 1-2 m of the river.

Figure 3.5: Example of a small stream at Tyndrum main mine site

The rivers and streams that drain the main site flow into a main river where it moves southeast and eventually spreads out on a floodplain area referred to as 'pond' in the OS map. The river then passes over a dam believes to be constructed during the mining period, to separate the galena and the sphalerite.

As explained by MacKenzie & Pulford (2002), the dam has a height of about 2 m and acts as a sediment trap and the area behind the dam is now entirely filled with sediment. Analyses of the riverbed sediments before and after the dam show that the less dense sphalerite flows over the dam, leaving the galena deposited on the bottom of the river.

Within the Tyndrum Main Site, samples of water, peat soil and tree bark were collected in order to study the mechanisms of dispersal of Pb and Zn, which will be discussed further in the following chapters. The tree bark samples represent atmospheric dispersal within most of the western side of the mine, while the peat cores signify the dispersal surrounding the eastern area, where trees are limited, as well as the SSD as mentioned earlier. The peat cores also provide useful information on the time of deposition using the ^{210}Pb dating technique. This will be explained in detail in subsection 3.3.6:Gamma Spectroscopy. The dispersal via fluvial transport from within the mine was investigated from the water samples with a sampling programme, which extended 25 km downstream of the mine site, as explained in the following subsection.

3.1.2 Outer Tyndrum Site

This section focuses on the next sampling area, which covers 25 km of the river system beginning from the small river forming the outflow from the Tyndrum area, after the confluence with Crom Allt. The sampling ends on the River Dochart, just before the Falls of Dochart, close to the village of Killin. This aspect of the research focussed on collecting river water, suspended particulate material and sediment samples, with the objective of investigating the dispersal of Tyndrum waste via fluvial transport. After flowing south from Tyndrum, the Crom Allt joins the larger River Fillan, which has a confluence with a major tributary, the River Cononish, just south of Tyndrum. The sampling locations cover a stretch of about 25 km, starting at a point on the River Fillan as shown in Figure 3.6. Sampling then continued at the confluence with the River Cononish.

At Crianlarich, the river turns eastwards into Loch Dochart, which has a length of about 1 km and width of about 250 m. After draining from Loch Dochart, the river discharges into a larger lake, Loch Iubhair, which has a length of approximately 2 km and width of about 500 m. The river system then narrows down into the River Dochart. Sampling ended approximately 2 km before the river enters the Falls of Dochart at Killin.

The River Dochart receives input from a network of many smaller tributaries between Loch Iubhair and the Falls of Dochart. The river water samples and riverbed sediments were collected at locations chosen based on a combination of ease of access and safety considerations. A riverbank core was also collected from the shore of Loch Iubhair. Further details on the sampling location of river water, sediment and the riverbank core are provided in sub-section 3.2.3: River Water and Sediments.

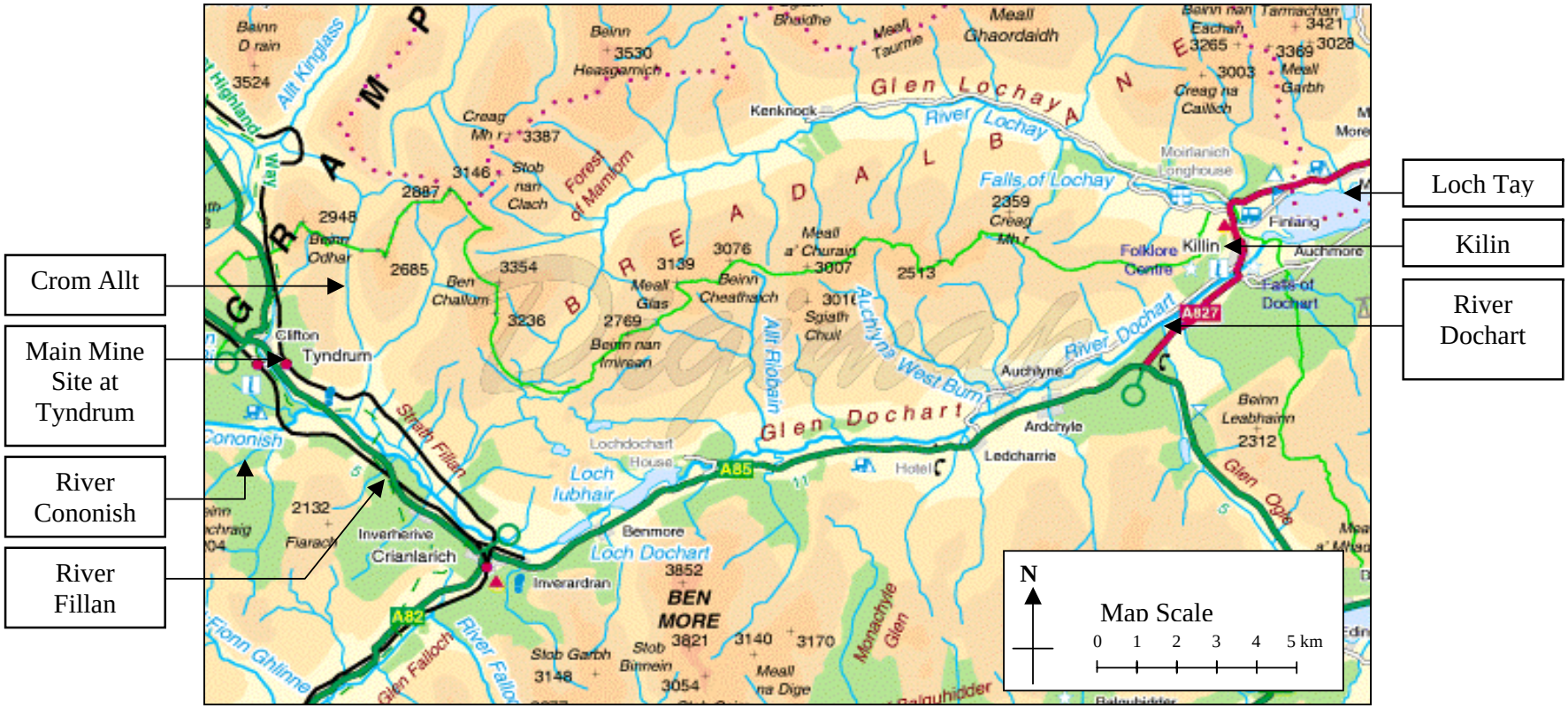

Figure 3.6: Map showing river system at Tyndrum main mine towards Loch Tay

3.2 Sampling and Analyses

This section will focus on explaining the selection of sampling points and the sampling procedures. It is divided into three sub-sections: tree bark, peat cores and river water and sediments.

3.2.1 Tree Bark

In this study, bark samples were collected from the Scots pine and Sitka spruce within the area surrounding the former mine. As depicted in Figure 3.7, the sampling points were chosen to cut across the site in a Northwest-Southeast transect, which is similar to the topography of the valley as described earlier in Chapter 2: Background of Tyndrum. This was done in order to investigate atmospheric dispersal along the valley relative to the prevailing wind direction, from the southwest (Patrick & Farmer (2007)).

The tree samples were identified based on their general characteristics and tree circumference for similar ages. Besides identifying tree species based on its physical appearance, the Tyndrum Stock Map (Figure 3.4) has provided added information and confirmation on choosing the right tree species on site.

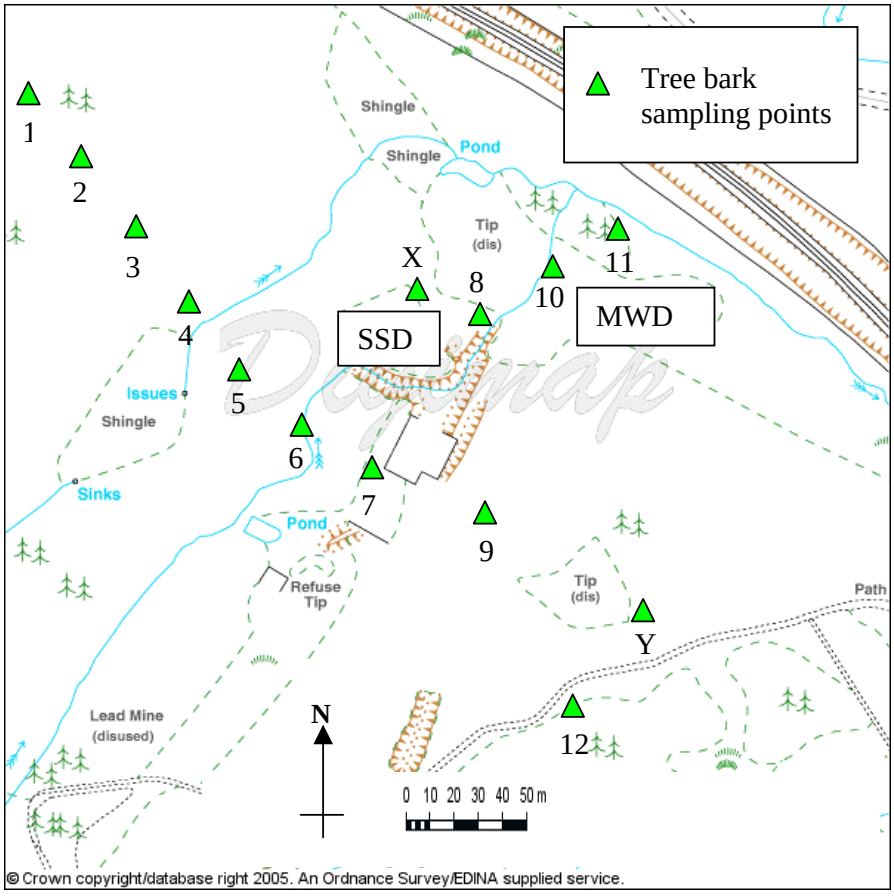

Figure 3.7: Map showing locations of Tree Bark Sampling Points

Tree bark samples 1-4 were collected from a thick forest stand, northwest of the site. Sampling then continued above the dumpsite area for Trees 5-7, maintaining the Northwest-Southeast transect pattern. Bark samples were also collected nearer to the Main Waste Dump (MWD) as well as beside the Small Side Dump (SSD), which is in an open area where the tree distribution is sparse.

Tree bark samples for Trees 10 and 11 were collected from the MWD and Tree 8 was at the SSD. Bark from Tree 9 was taken at the edge of another forest stand of the site and Tree 12 was within a forested area further south from the main site. A sample of Sitka spruce tree bark (shown as Y in Figure 3.7) was also taken at the site for comparison purposes that will be explained in the following section.

Bark samples of approximately 15 cm x 15 cm were removed using a stainless steel knife to a depth of approximately 1 mm (Tye et al. (2006)). The bark was collected from the NW and SE sides of each tree at a standard sampling height of 1.5 m above the ground. This height was chosen, based on previous studies, to avoid areas where soil particles may be splashed onto the trunk during periods of rainfall and reduce the influence of relative source position (Bohm et al. (1998); Wolterbeek & Bode (1995)). Lichens and mosses on bark surfaces were also included in the samples as the study aims to determine the physically trapped elements on the tree bark surfaces. Figure 3.8 shows a Scots pine bark that has been partially removed on the right side. Sampling was done on all 12 trees from locations as shown in Figure 3.7 of the sampling map.

Another aspect of this study was the sampling of bark at various heights of a single tree. Acknowledging that previous studies use a standard sampling height of 1.5 m above ground for reasons mentioned earlier, the approach adopted in this research also included investigation of the vertical distribution pattern of metals in the bark of a single tree. Bark samples were taken from Tree X at heights of 0.5 m, 1 m, 2 m, 3 m, 4 m and 5 m above ground. Samples were taken on both the NW and SE sides. Additional samples of pine needles, pinecones and twigs from the heights of 5 m and 7 m were also taken from Tree X, for the purpose of height comparison.

Figure 3.8: Scots pine bark

Another set of samples was taken from two trees of a known planting year. According to the Tyndrum Stock Map (Figure 3.4), the Scots pine trees at this site were planted in 1891 and the Sitka spruce were planted in 1975. Bark samples were taken from a Sitka spruce tree at a small waste tip towards the southeast of the site, shown as Y. This was then compared to a Scots pine sample, Tree 12. The bark samples were taken from these two trees to compare particle accumulation on the bark surfaces of two trees of different ages, in order to investigate whether the particles on the tree bark are consistent with current atmospheric exposure or long-term accumulation.

Bark samples obtained from the sampling site were placed in polythene bags, sealed and labelled before being taken back to the laboratory for analysis. The samples were not washed because the aim was to measure the elements that were physically trapped on the surface of the bark, as well as chemically bound to the cell wall. At the laboratory, the bark samples were weighed before being air-dried, after which they were re-weighed and placed in an oven at a temperature of 105^{o}C for about four hours.

The oven-dried samples were pulverised to uniform size with a laboratory mill using a 2 mm aperture. The mill was thoroughly cleaned and dried after each grinding to avoid cross-contamination between samples. The bark samples were then dry ash and digested using nitric acid, before analysis for total metal content.

3.2.2 Peat Cores

The peat core samples were collected from eight locations within the main mine site as well as the adjacent area near the dam. The term "peat" is used here based on the Soil Science Society of America definition (SSSA (1997)): *"Organic soil material in which the original plant parts are recognizable"*. This should be distinguished from a peat soil, which is defined as *"An organic soil in which the original plant parts are recognizable. The sum of the thicknesses of the organic layers are usually greater than the thicknesses of the mineral layers"*. The Soil Survey of England & Wales defines a peat soil as having an O horizon at least 40 cm thick (Avery (1973)).

The main objective for collecting the peat core samples was to reconstruct the atmospheric dispersal of Pb and Zn contaminants based on temporal variations in deposition established by analyses of 1 cm increments of the cores in conjunction with ^{210}Pb dating method. The first four samples were collected from near the small side dump (SSD) within the main mine site and the rest were taken at locations east of the rail tracks near the dam.

Cores 1-4 were collected on 27th January 2005. As illustrated in Figure 3.9, the locations of Cores 2–4 were all focused around the SSD site. Core 1 on the other hand, was collected nearer the old mining track at the foot of the hill, separated from the SSD by a small stream.

The samples were collected by cutting around the edge of a square shaped monolith of soil using the spade and carefully extracting it from the ground to the maximum possible depth. The samples were collected no deeper than 10 cm as rock and large stones were encountered beyond this depth. Each monolith was approximately 18 cm (W) x 20 cm (L) x 10 cm (D) in dimension and was kept intact by immediately wrapping it tightly to retain its shape and vertical integrity.

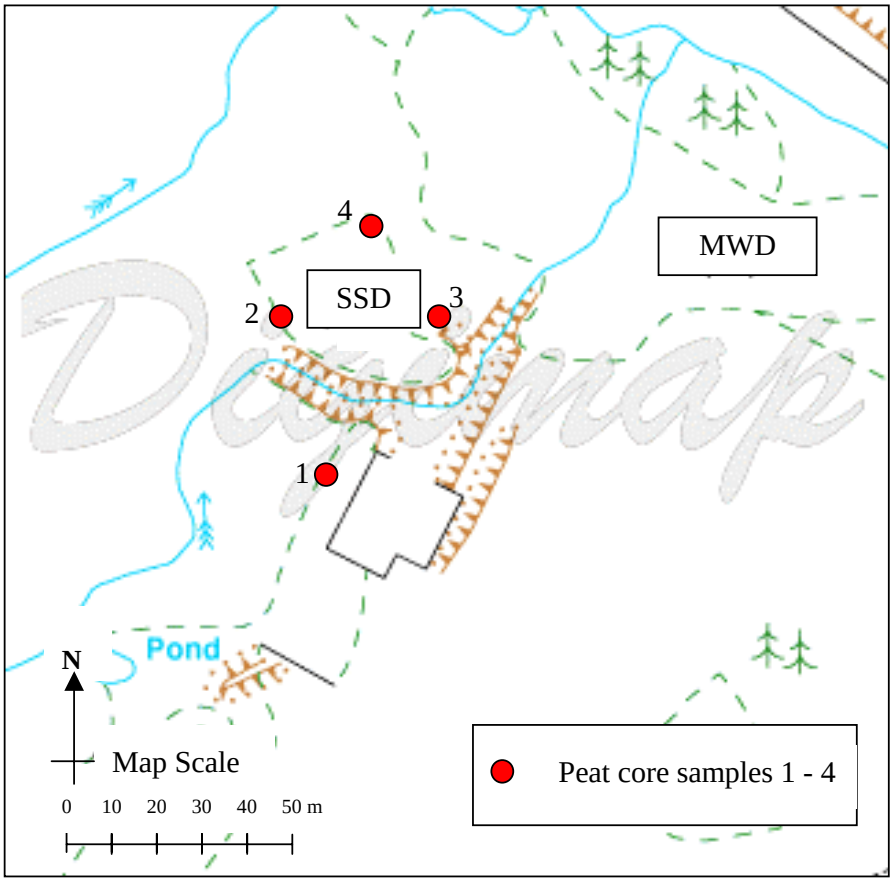

Figure 3.9: Map showing locations of sampling points for Peat Cores 1-4

The next four samples, Cores 5-8 were collected on 27th April 2005. Figure 3.10 show samples 5 and 6, which were collected nearer the dam, while samples 7 and 8 were from riverbanks downstream along the river. The samples within this area were collected using a plastic pipe of 15 cm length and 10.5 cm in diameter. At each location, the plastic pipe was hammered to the maximum possible depth, which was between 7 cm – 10 cm depth and the core extracted. Upon returning to the laboratory, the samples were placed in a cold room prior to laboratory analyses.

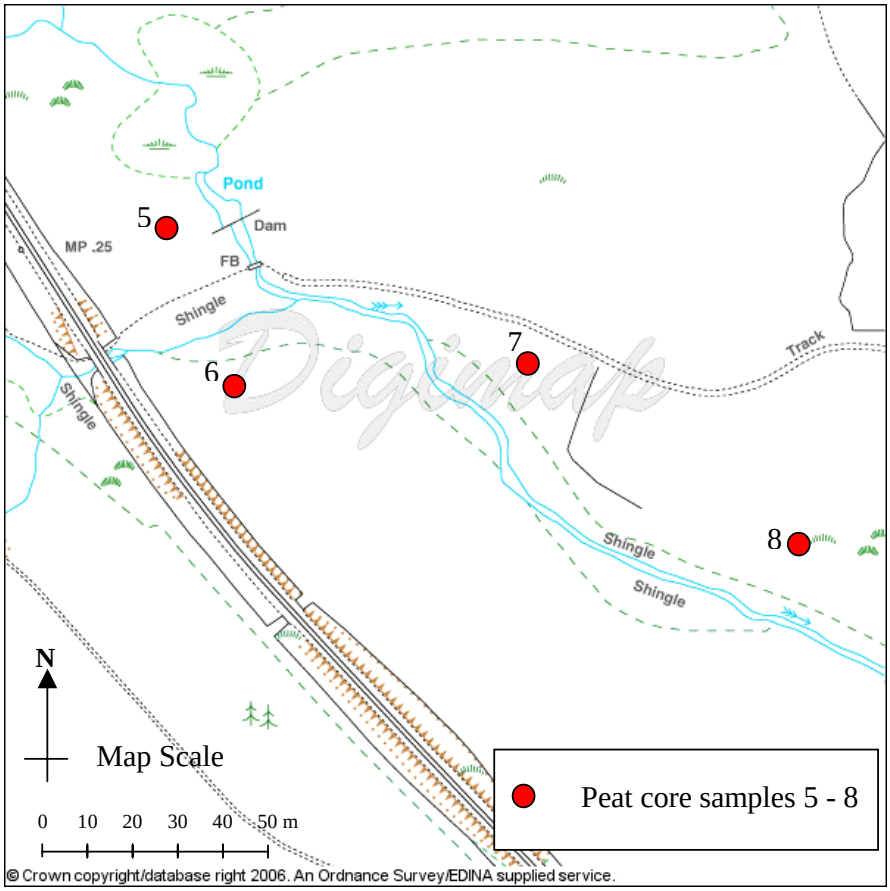

Figure 3.10: Map showing locations of sampling points for Peat Cores 5-8

In the laboratory, each core was carefully removed from the plastic wrappings and plastic pipes whilst keeping them as intact as possible. The cores were then carefully sectioned into 1-cm vertical increments. The individual sections were weighed and air-dried at room temperature. Once dried the cores were re-weighed and sieved using a 2 mm stainless steel sieve. The next step was the aqua-regia digestion process followed by Pb and Zn concentration analyses using the Perkin Elmer 1100B Atomic Absorption Spectrometer. Some of the samples were also analysed for ^{137}Cs, ^{210}Pb and ^{226}Ra by gamma spectroscopy analysis.

3.2.3 River Water and Sediments

This sub-section focuses on the collection of samples from the river system, including river water samples, suspended sediments, riverbed sediments and a riverbank core. Sampling focussed on two areas: (i) the complex of small streams draining the main mine site and (ii) the larger rivers which includes two lochs, extending some 25 km from the mine to Loch Tay. Figure 3.11 and Figure 3.12 illustrate the locations where samples were collected. A brief description and grid references for each of the sampling points are also included in Table 3.1.

The first samples collected in this part of the study were water samples from the network of streams within the mine site. The main objective of collecting these samples is to determine the metal concentration in the solution in order to evaluate contemporary dispersion into the Fillan/Dochart river system. As illustrated in Figure 3.11, twelve river water samples were collected from different locations within the mine area.

Sampling started from the far northwest side of the site where small streams flow through. Sample collection then continued at other streams including the largest stream flowing from the hillside through the dumpsites (MWD and SSD). The final sample was collected before the river enters the floodplain, northeast of the site.

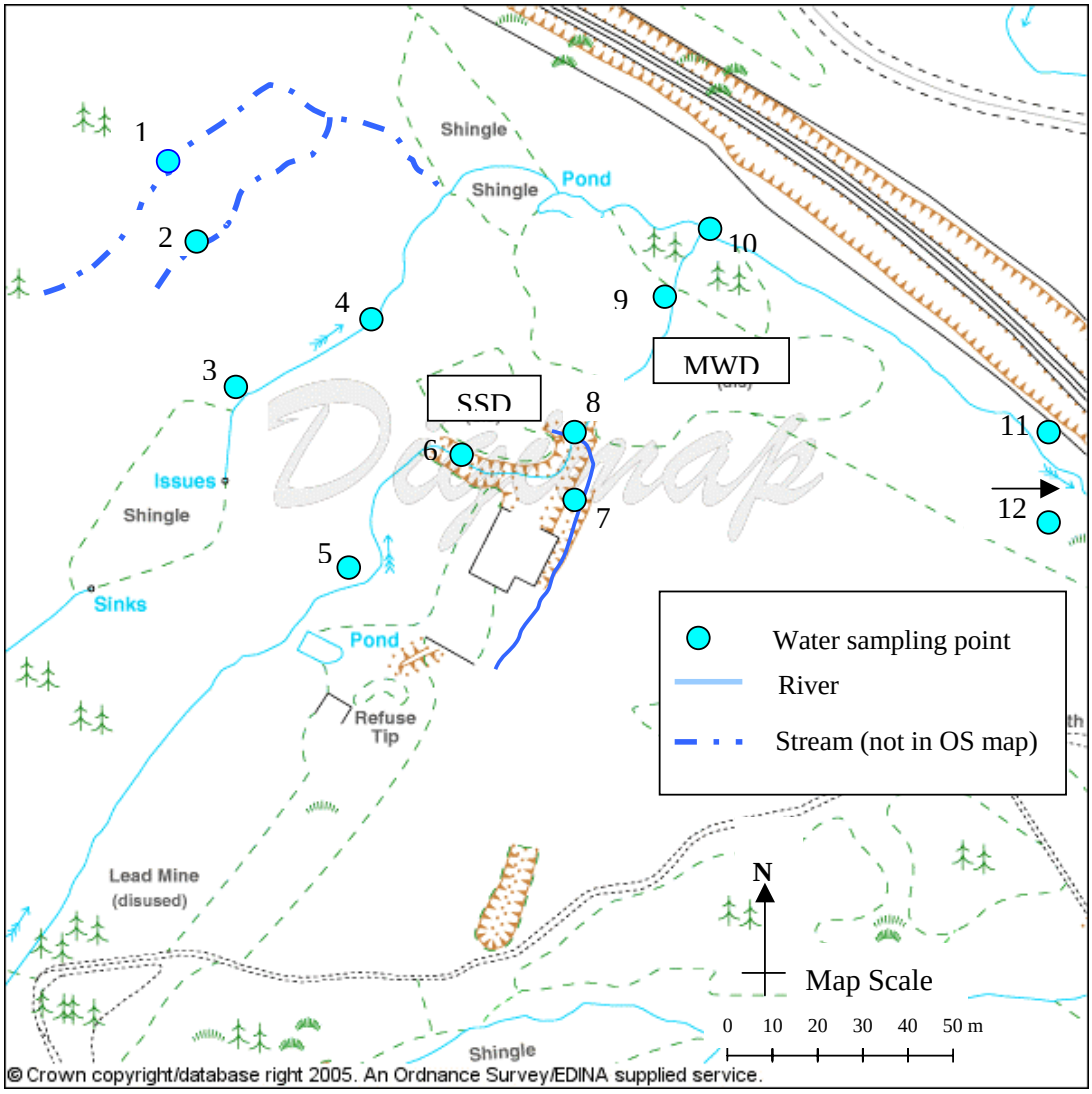

Figure 3.11: Map showing sampling points for River Water Samples 1-12

Sampling of these twelve sites was repeated on four different occasions in 27th January, 27th April, 25th August and 16th December of 2005. The river water samples were collected in 150 ml plastic bottles, which were thoroughly rinsed with river water twice prior to sample collection to eliminate cross contamination. The samples were carefully collected without disturbing the riverbed in order to reduce the possible collection of riverbed sediments along with the water samples. A second bottle was also collected at each site as a duplicate sample. The bottles were clearly labelled and kept in a cold room prior to laboratory analysis.

The analyses for these samples involved three different procedures. The first procedure was to directly analyse the total Pb and Zn concentration in the sample without any prior processes for the composite analysis of dissolved and suspended material in water. The concentration of both elements was measured using a Perkin Elmer 1100B Atomic Absorption Spectrometer (AAS). These samples will be referred to as 'original' samples. The original samples are then split into two sub samples one of which was filtered through a 0.2 μm filter. The filtrate was collected and the metal concentrations analysed using the AAS. Meanwhile, the second sub sample was acidified by adding two drops of 11.65M Nitric Acid. This was done to lower the pH of the sample before analysis for total Pb and Zn concentrations. This method was applied to all four sets of river water samples that were collected from January – December 2005. All of the analyses were carried out in duplicates. The results between the three analyses will then be compared to each other in an attempt to determine the metal concentration in total solution phase.

The second batch of river water samples was taken from the Rivers Fillan and Dochart for the purpose of analysing the metal concentrations in colloidal phase and solution phases in the water body. The samples were later filtered to attain its suspended materials for the analysis of the colloidal phase and its filtrate for determining the solution phase. There were eight sampling sites in total as depicted in a sketch of the sites in Figure 3.12 and the grid references are given in Table 3.1.

Samples were collected on 22nd May 2006 and 14th March 2007. Samples of 5 litres to 10 litres volume were collected at each site, since earlier trial studies using smaller volumes of 1 litre proved to be too small for the analysis of either dissolved metal concentration or concentrations in suspended particles. The river water samples in this section were filtered through a two-step filtration process. The first filtration was through a 1.2 μm glass microfibre filter and the second through a 0.2 μm nylon membrane filter. A motorized vacuum pump was used in assisting the filtration process.

Prior to the filtration process, the filters were first weighed. After the samples had been filtered, the respective filters were placed in desiccators overnight to remove excess water. The filters were then re-weighed to determine the weight of suspended solids collected.

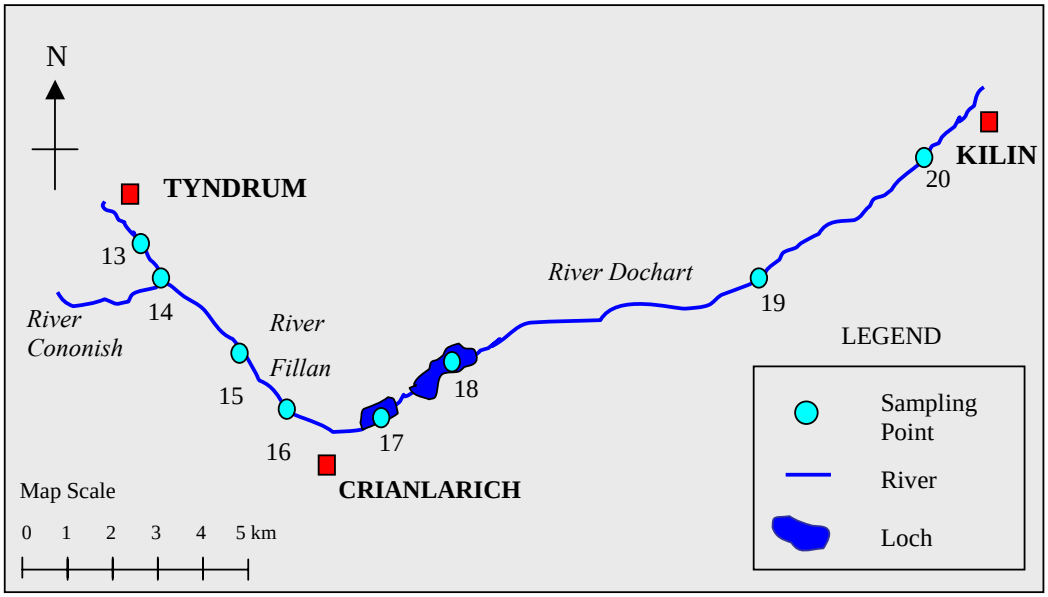

Figure 3.12: Map of sampling locations of River Water and Sediment Samples 13-20

The filters and suspended solid material were then dissolved using the wet ash procedure as explained in 3.2.3 Nitric Acid Digestion. The digests were then analysed for Pb and Zn using a Perkin Elmer 1100B atomic absorption spectrometer. The digested solids from the filters were also analysed for Pb isotope ratios using a VG Plasma Quad 2 Inductively Coupled Plasma-Mass Spectrometer. The third batch of samples collected from the river system comprised riverbed sediments and one of the objectives of this phase of the study was to determine the metal concentrations within different size fractions of the sediment, specifically the coarse and fine sand and silt fractions. The sediments were also analysed for stable Pb isotope composition in an attempt to identify the origin of the Pb in the sediment at different locations.

The riverbed sediment samples were collected from similar locations to the river water sample, where bed sediment was reasonably accessible. The first set of samples (22nd May 2006) was collected at six locations and the second (14th March 2007) at only four locations. This was because two of the locations were not accessible at the time of sampling due to floodwater conditions. The grid references of sampling locations for the riverbed sediments are given in Table 3.1. Some of the samples include sediments nearer to the banks or further to the middle where the river level is shallow. All of the riverbed sediment samples were collected using a stainless steel trowel and placed in polythene bags and sealed and labelled. The labelled bags were then placed in a cold room prior to laboratory analyses.

Table 3.1: Sampling point grid reference, sample codes and sampling protocols for river water and sediment samples.

Grid Reference	Sampling Points	River Water	Sediment (2006)	Sediment (2007)
334297	13	√	√	X
340291	14	√	√	√
350288	15	√	X	X
358281	16	√	√	√
406256	17	√	√	√
425267	18	√	√	√
504286	19	√	X	X
556314	20	√	√	X
Notes				
√	Available			
X	Unavailable			

The riverbed sediments were weighed wet and then air-dried at room temperature. Once dried the sediments were re-weighed until constant weight and separated into different particle sizes. This was achieved by dry sieving the samples into coarse sand (> 180 μm), fine sand (53-180 μm) and silt (< 53 μm) fraction. The samples were analysed for total metal content after aqua-regia acid digestion. The methodology for this analysis is explained in sub-section 3.3.3: Aqua Regia Digest.

Finally, a riverbank core was obtained from the shore of Loch Iubhair. The main purpose of collecting the riverbank core was to attempt to establish the historical pattern of metal deposition in the sediment and to relate this, if possible, to mining and ore processing operations at Tyndrum and to the sedimentary record in Loch Tay (Farmer et al. 1997). The core dimensions were adequate to provide sufficient material for metal analysis and for ^{210}Pb dating. The location of the riverbank core is indicated as sampling point 17 in Figure 3.12. A vertical section was extracted on the exposed bank of the loch using a steel coring tray and a trowel, as shown in Figure 3.13 .The dimensions of the core were 7 cm (W) x 15 cm (D) x 34 cm (L). After extraction of the sediment, the tray was carefully wrapped and labelled before being placed in a cold room prior to laboratory analysis.

The riverbank core was carefully removed from the tray and sectioned into 2-cm vertical increments. The individual sections were weighed and air-dried at room temperature. Once dried the samples were re-weighed until constant weight and sieved using a 2 mm stainless steel sieve. A 20 g sub sample was removed for gamma spectroscopy analysis and a separate sub sample was subjected to aqua-regia digestion followed by Pb and Zn analyses by AAS. Stable Pb isotope ratios were also analysed for these samples using an Agilent 7500ce ICP-MS. The methodologies for the various laboratory analyses are explained in Section 3.3 Methodology of Laboratory Analysis.

Figure 3.13: Sampling of riverbank core at Loch Iubhair

3.3 Methodology of Laboratory Analysis

This section explains the methods used during the analytical procedures in the laboratory. All of the samples were analysed in duplicates and some in triplicates where possible. In the soil analysis, certified reference material (CRM) LGC 6135 was used to ensure verification of the data obtained from the experimental material. All samples were analysed using the Atomic Absorption Spectrometry (AAS), although the preparation of the samples prior to using the AAS depended on the type of sample.

3.3.1 Total Organic Content – Dry Ash

The preparation procedure for metal concentration measurements usually requires initial decomposition of the organic matter in samples. This procedure is carried out primarily to avoid adverse effects of the organic matter on the equipment, due to its high sensitivity. At the same time, the combustion of organic matter also allows calculation of the fraction of organic and inorganic material contained in a particular sample. In this research, most of the solid samples were subjected to organic decomposition to detect the mineral and organic fractions. Samples prepared for Pb isotope analyses, such as riverbed and riverbank sediments, were dry ashed prior to analyses due to the sensitivity of the ICP-MS.

Dry ashing is described as the heating of a sample, using a burner or a muffle furnace, resulting in combustion of the organic component leaving the inorganic material as ash. The procedures for dry ashing or Loss On Ignition (LOI) are explained as follows;

1. Silica basins were oven-dried at 110 °C for an hour prior to usage
2. Basins were then left in a desiccator to cool
3. Once cooled, the basins were weighed on a four figure balance

4. Subsample of mass approximately 5 g of air-dried soil or (2 g for bark) were weighed accurately into the basins, which were returned to the oven and left overnight
5. The basins plus sample were cooled in a desiccators again and re-weighed to give the weight of oven dried sample
6. Samples were then pre-ashed by placing a lid on the basin and heated using a Bunsen burner. This was done until no more smoke was evolved
7. The basins were then placed in a muffle furnace set at 550 °C for 5 hours
8. Samples were left to cool in the furnace overnight
9. Once removed from the furnace, the basins plus samples were placed in desiccators
10. The basins plus samples were then re-weighed to give the weight of the ash sample

The percentage loss on ignition (LOI%) was calculated using the following equation:

$$\text{LOI \%} = \frac{\text{weight of oven dry sample} - \text{weight of ignited sample}}{\text{weight of oven dry sample}} \text{ x } 100$$

(2.1)

3.3.2 Nitric Acid Digestion

Nitric acid digestion was used in this study prior to measuring total metal content by AAS. The first part of this section focuses on the nitric acid digestion of the filtered suspended solid samples. The following part will deal with the tree bark samples. It is worth mentioning here that nitric acid digestion of a sample that has not undergone any prior procedure is sometimes referred to as a 'wet ashing' process. The definition of wet ashing is similar to that of dry ashing except that it uses nitric or sulphuric acid, at high temperature, to decompose organic matter. In the case of the suspended matter that had been recovered by filtration, the organic component of the suspended solids is decomposed at the same time as the filter papers and filter membrane.

Thus, the acid digestion meets the criteria to be referred to as 'wet ashing'. However, unlike in dry ashing, the weight of the organic component is not determined during the procedure.

Suspended solids

The filter papers in this study were weighed prior to, and after, the filtration process to determine the weight of suspended matter as part of the procedure for analysis of metal concentrations in the suspended particles as follows;

1. The filters were placed in beakers and immersed in 5 ml of 1.6 M HNO_3
2. The beakers were heated on a hot plate at 120^{o}C for 30 minutes, stirring occasionally until the acid solution had totally evaporated
3. Once cooled, the residues were dissolved in 10ml of 8 M HNO_3
4. The digests were then filtered through Whatman No. 541 filter paper and made up to the mark in 50 ml volumetric flasks with washings
5. The samples were then ready to be analysed for total metal content by AAS.

Tree Bark

The tree bark samples were digested in nitric acid following dry ashing in the furnace. In this instance the tree bark samples are considered to be acid digested after being dry ashed. The procedures following the dry ash process for the bark samples are as follows;

1. The ashed samples from the furnace were dissolved with 1.6 M HNO_3 solution
2. The samples and solution were left to stand for a few minutes to allow the mixture to equilibrate
3. The digested samples were then filtered through a Whatman No. 541 filter paper into a 100 ml standard volumetric flask with washings.
4. The samples were then made up to the mark with 1.6 M HNO_3 solution.
5. The samples were then ready to be measured for total metal content using the AAS.

3.3.3 Aqua Regia Digest

Aqua regia refers to a solution comprising a mixture of 3:1 hydrochloric acid and nitric acid. This was prepared by adding three parts of 6M HCl to one part of 16M HNO_3. In this study, the riverbed and riverbank sediment as well as peat core samples were digested in aqua-regia prior to analysing metal concentrations by AAS. The procedures are as follows;

1. Approximately 0.25 – 0.5 g of dry sample was weighed on a detachable spatula using a four-figure balance. The spatula was re-attached to its handle and the sample was then placed at the bottom of a digestion tube. The handle of the spatula has to be longer than the tubes for this procedure, which must be done carefully to ensure that the sample does not attach to the sides.
2. 10 ml of aqua-regia was then dispensed into each tube and the tubes were left to stand overnight to allow the mixture to equilibrate.
3. The tubes were then placed in the digestion block and the temperature set at 125^{o} C.
4. The extraction unit was then switched on for at least three hours, until the tubes were clear of the brown NO_2 gas.
5. After the tubes had cooled, 10 ml of deionised water was added to each tube.
6. The digests were then filtered through a Whatman No. 50 hardened filter paper into 50 ml volumetric flasks.
7. The samples were then made up to the mark with deionised water and were then ready to be measured for total metal content using the AAS.

3.3.4 Total Metal Content – Atomic Absorption Spectrometry (AAS)

Total metal content of samples were determined by Atomic Absorption Spectrometry. The instrument model used was the Perkin Elmer 1100B. The instrumental parameters for Pb and Zn are as shown in Table 3.2.

Table 3.2: Instrumental Parameters for Pb and Zn

ELEMENT	**Pb**	**Zn**
Wavelength (nm)	283.3	213.9
Slit width (nm)	0.70	0.70
Signal Type	Atomic Absorption Spectrometry	Background Corrected Atomic Absorption Spectrometry
Signal Measurement	Time Average	Time Average
Flame Type	Air / C_2H_2	Air / C_2H_2
Oxidant Flow (L min^{-1})	2.5	2.5
Fuel Flow (L min^{-1})	2.0	2.0

Total metal content includes all metals, organically or inorganically bound, both dissolved and particulate. According to the American Public Health Association (1992), unless samples are colourless, transparent, odourless, single phase, and have turbidity < 1 Nephelometric Turbidity Unit, they will require digestion before being analysed using an Atomic Absorption Spectrometer (AAS).

The principle of the AAS instrument is as explained below;

1. The sample solution is aspirated through a flame in order to generate the element to its atomic form.
2. Light from a hollow cathode lamp is passed through the flame and the atom absorbs the light (atomic absorption) and enters an excited state. The hollow cathode lamp contains the element to be measured.
3. During the atomic absorption there is a reduction in the intensity of the light beam, which can be measured, and directly correlated with the concentration of the elemental atomic species.
4. The measurements are carried out, by comparing the light absorbance of the unknown sample with the light absorbance of known calibration standards.

Standard solution for Pb and Zn

In measuring total content of Pb and Zn by AAS, standard solutions for each metal were first prepared. The Pb standards had concentrations of 5 ppm, 10 ppm, 15 ppm, 20 ppm and 25 ppm, while those for Zn were 1 ppm, 2 ppm, 3 ppm, 4 ppm and 5 ppm. The standard solutions were prepared as dilutions of primary Analar grade standard solutions of 1 x 10^3 ppm concentration for both Pb and Zn. The standards were prepared in matrices that corresponded to those of the samples. The relevant calculations and procedures for preparation of the standards are included in the appendix section. The sensitivity of the atomic absorption spectrometer was checked once the position of the flame relative to the light beam was adjusted to give maximum absorbance reading with the top standard solution and the mix of gases in the flame was modified to give the optimum reading. The atomic absorption spectrometer was then calibrated with the standard solutions and the samples were analysed, checking the calibration after every 10 samples.

Detection Limit (DL)

The detection limit is defined as the lowest concentration that can be clearly differentiated from zero. The standard procedure for establishing detection limits by flame AAS is as follows;

1. A standard solution of known concentration of each element is prepared. In this study, the 15 ppm Pb standard solution and 3 ppm Zn standard solution were used.
2. The instrument is calibrated with the range of standard solutions (as mentioned in the previous paragraph). Using standard solution of 15 ppm for Pb and 3 ppm for Zn, ten readings are made with a blank (solvent only) between each standard reading.
3. The average of the blank reading immediately before and immediately after each standard was calculated and subtracted from the standard reading. The standard deviation of each reading is noted.
4. The mean from the ten standard deviation readings was used in the calculation for the detection limit as shown in the following;

Detection Limit (DL) = 3 x mean of standard deviation (10 readings) (2.2)

Detection range may be extended downward by scale expansion or by integrating the absorption signal over a long time, and upward by dilution of sample, using a less-sensitive wavelength, rotating the burner head, or by linearising the calibration curve at high concentrations.

3.3.5 Lead Isotope Ratio – Inductively Coupled Plasma Mass Spectrometry (ICP-MS)

Determination of lead isotope ratios analyses was conducted in a clean laboratory at the Scottish Universities Environmental Research Centre (SUERC) in East Kilbride. The $^{206}Pb/^{207}Pb$ atom ratios were determined by inductively coupled plasma mass spectroscopy (ICP-MS). The samples used in this method had undergone dry ashing or acid digestion to remove organic components prior to the analyses. The reason for the pre-removal is because the organic matter may interfere with the ICP-MS system.

The ICP-MS is a type of mass spectrometer that is highly sensitive and is capable of analysing a range of metals and several non-metals at concentrations below one part in 10^{12} (1 ppb). The instrument design is based on coupling together inductively coupled plasma, as a method of producing ions (ionisation), with a mass spectrometer as a method of identifying and detecting the ions.

The general procedures of the ICP-MS analysis carried out during this study were as follows;

1. Samples were diluted in 8M HNO_3 and diluted in an appropriate range of 20 – 40 ppb concentration.
2. Due to this requirement, each sample had therefore been previously analysed for its concentration by AAS and then diluted accordingly.
3. Blanks and lead standards were also included in each ICP-MS analysis run and nitric acid washes are used in between each measurement.
4. Samples were injected into the instrument, normally by an auto sampler. The samples were placed in a sequence, which included the blanks, lead standards and nitric acid washes.
5. In the ICP-MS instrument, samples go through an atomisation interface and pass through a glass tube along with an argon carrier gas. The sample is then exposed to a radio frequency electric current, which acts to produce ions. The ions collide with other argon atoms, forming an argon discharge, or plasma.

6. Decreased pressure, induced by vacuum pumps, causes a fraction of the ions to pass through a series of cones into the quadrupole mass filter of the mass spectrometer.
7. The ions are separated on the basis of their mass-to-charge ratio (m/e) and those of a specified ratio impinge on a detector, which produces a signal proportional to the concentration. The ability to filter ions on their mass-to-charge ratio allows the ICP-MS to supply isotopic information, since different isotopes of the same element have different masses. Hence, the isotopic ratios can be calculated and samples can then be identified and characterised. In this study, the stable isotopes of interest were ^{206}Pb, ^{207}Pb and ^{208}Pb.

3.3.6 Gamma Spectroscopy

The ^{210}Pb dating method is used to determine the accumulation rate of sediments within a core profile. In this study, samples of peat and riverbank sediments were analysed for ^{210}Pb, ^{226}Ra and ^{137}Cs by gamma spectrometry. The general procedures involved in the gamma spectroscopy were as follows;

1. A 20 g subsample of dried sediment or peat was weighed into a 47 mm diameter polystyrene petri dish, which was then sealed with Araldite for counting.
2. The samples were stored after being sealed for at least three weeks to allow secular equilibrium to be established between gaseous ^{222}Rn ($t_{½}$ = 3.82 days) and its parent ^{226}Ra ($t_{½}$ = 1600 years). Due to the low energy of the 46.7 keV gamma emission of ^{210}Pb, care must be taken to ensure that there are no significant differences in chemical composition or density between samples or between samples and standards. In the present case, care was taken to ensure that samples within a set, and their corresponding standards, were sufficiently similar in composition and density that variations in self absorption were minimal.

3. Standards were prepared by "spiking" peat or sediment, from a depth at which unsupported ^{210}Pb and ^{137}Cs were not detectable, with known activities of the nuclides of interest, using solutions prepared from primary standards obtained from Amersham International. 20 g samples of the standards were prepared in the same way as the samples and their gamma spectra were recorded using the same petri dishes and counting geometries as the samples. Detection efficiencies for the nuclides of interest were calculated on the basis of the spectra for the standards.
4. All measured count rates for the samples were corrected for background, and activities were calculated using the defined detection efficiencies for the radionuclides.
5. The LEGe detector used in this study was housed in a graded Pb–Cd–Cu shield to minimise background. Gamma spectra were recorded using an EG&G Ortec ADCAM unit and analysed using the Ortec software package GammaVision 2.

The model that is used to calculate the sedimentation rate in this study is the CIC (Constant Initial Concentration), as discussed in Chapter 2.

3.3.7 Scanning Electron Microscopy (SEM)

The Scanning Electron Microscope is a microscope that uses electrons rather than the conventional microscope that uses light to form an image. The SEM has a large depth of field, which allows a large amount of the sample to be in focus at one time. The SEM also produces images of high resolution, which means that closely spaced features can be examined at a high magnification. The combination of higher magnification, larger depth of focus, greater resolution, and ease of sample observation makes the SEM one of the most preferred analytical instruments.

Principles of SEM

An SEM focus scanned electron beam to produce images of the sample, both top-down and, with the necessary sample preparation, cross-sections. The primary electron beam interacts with the sample in a number of key ways:-

1. Primary electrons generate low energy secondary electrons, which tend to emphasise the topographic nature of the specimen
2. Primary electrons can be backscattered which produces images with a high degree of atomic number (Z) contrast.
3. Ionised atoms can relax by electron shell-to-shell transitions, which lead to either X-ray emission or Auger electron ejection. The X-rays emitted are characteristic of the elements in the top few μm of the sample

The extremely high magnification images together with localised chemical information mean the instrument is capable of solving a great deal of common industrial issues such as particle analysis, defect identification materials and metallurgical problems. In this study the SEM signals are used to recognise and detect the elemental composition of a particular sample.

CHAPTER FOUR

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4.0 RESULTS AND DISCUSSION

This chapter presents the results for each of the different samples investigated in this study. It is separated into three sections dealing with tree bark, peat cores and river water and sediments. The results are discussed within each section and data tabulated in the appendices accordingly.

4.1 Tree Bark

The results of the tree bark sample analyses can be divided into 3 separate sub-sections. The first sub-section focuses on the results for bark samples taken from the same height of twelve trees. The second sub-section describes the results for bark samples, needles, twigs and cones taken from different heights of the same tree. The final sub-section explains results for bark samples from two different tree species planted in different years. As previously explained, each set of results discusses the distribution of Pb and Zn on both the SE and NW sides of each tree. It is worth pointing out that the twelve sample trees (apart from Trees 9 and 12) have the SE side directly facing the mine dumpsites as clearly shown in the sampling map for tree bark in Figure 3.11

4.1.1 Side Facing Aspects

Figure 4.1 shows the results for the bark samples taken from twelve trees from various locations in the vicinity of the mine, where samples were collected at 1.5 m height on the NW and SE sides. The twelve trees are separated to two main groups, the first of which are those from area A, which indicates that the trees are within 50 m of the main waste dump (MWD) as well as the small side dump (SSD). This area has trees 8, 10 and 11. The second group comprising nine trees are in area B, situated between 50 m to 250 m away from the dumpsites. The approximate distance of the trees from the point source are as indicated on the x-axis of Figure 4.1. Samples to the left of centre are from the NW side of trees, while those to the right of centre show corresponding data for the SE side of the same trees. The results reveal that the Pb concentration ranges between 10 mg kg^{-1} and 1850 mg kg^{-1} and the Zn concentration between 10 mg kg^{-1} and 140 mgkg^{-1}.

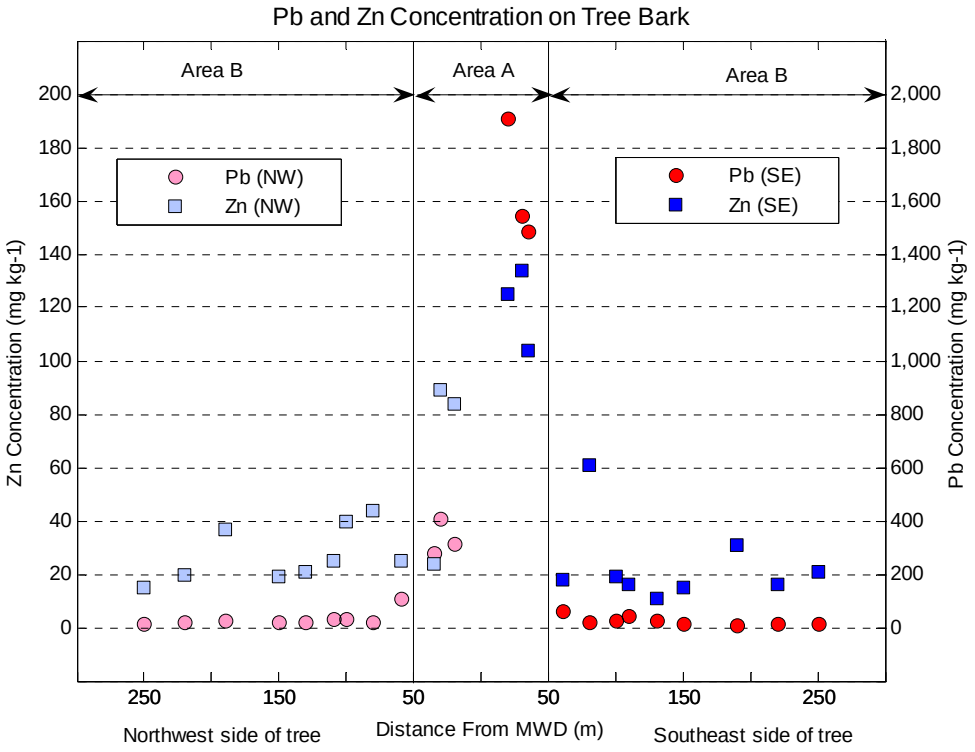


Figure 4.1: Metal concentrations in tree bark collected from a height of 1.5 m above ground level.

As shown in the figure, bark samples from area A show high Pb concentrations, with a range of 300 mg kg^{-1} to 1850 mg kg^{-1}, which are much higher than those for trees in area B, where the range was 20 mg kg^{-1} to 100 mg kg^{-1}. Zn similarly shows substantially higher concentrations in bark from trees from area A, with a maximum concentration of approximately 140 mg kg^{-1}, whereas the highest concentration observed in area B was 61 mg kg^{-1}. It is also worth saying that Pb and Zn concentration on the SE side are much greater than those in the NW side within 50 m, but not at greater distance.

The results are therefore consistent with the conclusion that very high levels of contamination are restricted to trees located within 50 m radius of the dumpsites. As a result of being at a closer distance to the waste, these trees have higher Pb and Zn concentrations. In addition to distance, another contributing factor to the observed distribution could be that trees in area B are situated in a much denser forest stand compared to area A and this may restrict aerial dispersion of the contaminant metals.

Figure 4.2 shows the Pb/Zn concentration ratio for all twelve trees, with the NW and SE on either side of the graph, as before. Area A shows that the trees located closer to the MWD and SSD are receiving mine waste greatly enriched in Pb, with Pb/Zn ratios of 5 to 20. When comparing the two sides, the NW side has an average Pb/Zn ratio of 7 while its SE side show an average Pb/Zn ratio of 15. Area B meanwhile shows a much lower Pb/Zn average ratio of 1.2 on the NW side and 1.9 on its SE side. The Pb/Zn ratio seems to be systematically higher on the SE side than the NW side. This could probably suggest that Zn is experiencing leaching mainly on the SE side.

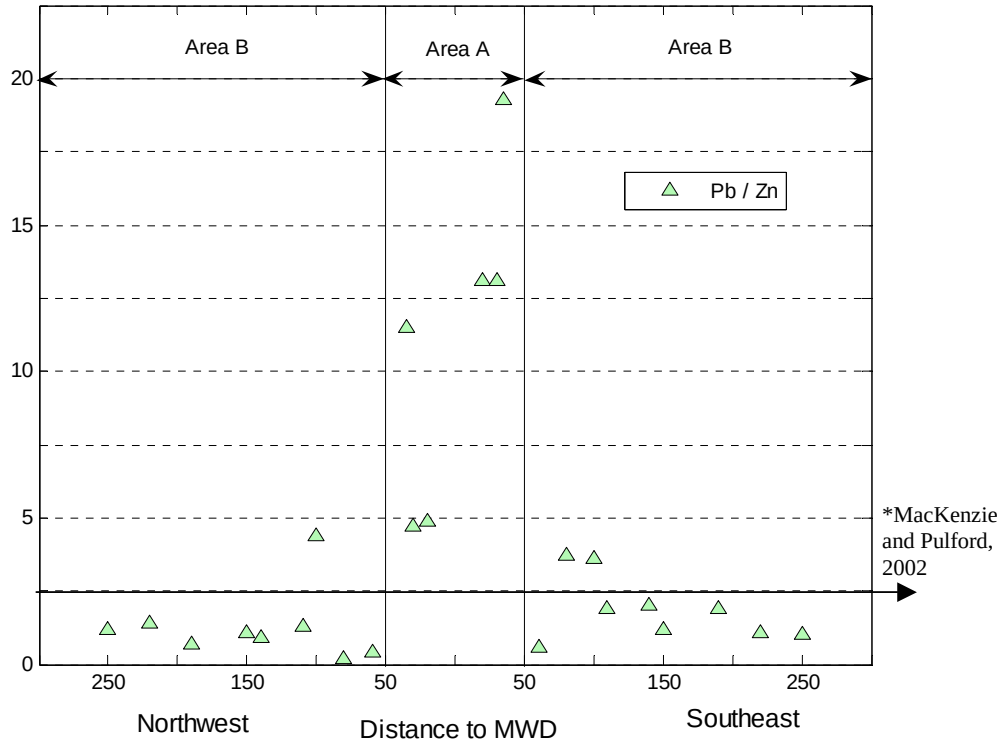


Figure 4.2: Pb / Zn Ratio

The results have clearly shown that the metal concentration collected from the bark surfaces in area A have higher Pb/Zn ratios than area B. Based on this observation, several arguments are raised. Assuming that trees in area A are receiving direct aerial dispersal from the waste, it would be expected that the Pb/Zn ratio to be about 2.4, similar to that of the waste material (*MacKenzie and Pulford, 2002). In this case however, due to the higher Pb/Zn ratio, one assumption would be that the waste material on the bark surfaces is experiencing higher loss of Zn due to its higher solubility.

As mentioned previously in Section 2.2.2, Schulz et al. (1999) reported in their study that the atmospheric deposition processes involve both wet and dry deposition. Area B may not be experiencing similar stem flow as area A, due to canopy resistance owing to the density of trees within its area. Greater stem flow could be occurring on trees within area A. Hence, Zn within the material in area B does not experience the same rate of weathering, thus giving a lower Pb/Zn ratio compared to area A, similar to that of the waste material.

Another possible explanation is that the waste material itself might be experiencing weathering process altering its Pb/Zn ratio. This is arguable as analysis of the waste material was not included as part of the investigation of this current study. The waste material may contain different Pb/Zn ratios within its profile, with surface material, which is subject to atmospheric dispersal, having a different ratio from material at depth. In this case, area A might be receiving the current top material while Area B, situated at a further distance, is still retaining previous waste material of a lower Pb/Zn ratio.

Attempting to understand the airborne material collected on the bark surfaces based on its Pb/Zn ratio shows great complexity. Further investigation is needed in the future to confirm or refute the assumptions. Nevertheless, on the aspect of aerial dispersal, it is obvious that the material collected on the surfaces is greatly enriched in Pb mainly within the dumpsites and that this effect reduces with distance. The side facing aspects of the trees also gives several insights into the dispersal pattern of the former mine.

Figure 4.3 shows the SE/NW ratio of each contaminant for the twelve tree samples. It is observed that Pb and Zn concentrations are greater on the SE sides within area A. The results are as expected since the SE sides of trees within area A face the dumpsites. This shows that the contamination on the bark surfaces is greatly influenced by wind-blown occurrences. The average SE/NW ratio for trees in area B was 1.4 for Pb and 1.0 for Zn. The results reflect a fairly even distribution of the contaminants on both sides. It is worth mentioning that Trees 9 and 12 are highlighted in the figure as they were not part of the northwest-southeast sampling transect. Both display slightly different trend of SE/NW ratio compared to the rest. The reason for this may be due to the position of the trees further to the east of the dumpsites. These trees are therefore subjected to influence from other possible background source or unknown waste tips.

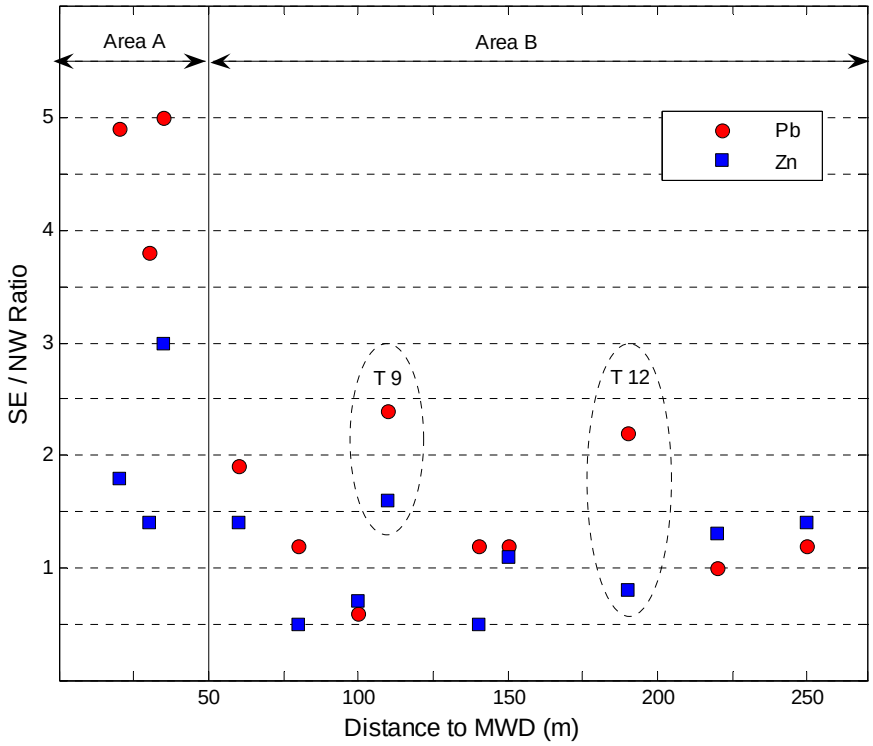


Figure 4.3: Ratio of SE / NW for Pb and Zn

The results for this section show clear trends between distances of the tree samples relative to the point source of MWD and SSD. Area A reveals elevated levels of Pb and Zn in tree bark compared to trees beyond 50 m in area B. This indicates that the airborne dispersal of the contaminants is localised within 50 m distance, beyond which the heavy metal concentrations greatly decrease. The effect of airborne dispersal is indicated by the difference between metal concentrations on each side of the trees, with higher concentration of contaminants on the SE side within area A. The Pb and Zn distribution in area B on the other hand reveals a similar distribution of contaminants on both sides. There also exist several contradicting assumptions relating to the Pb/Zn ratio, which clearly require further investigation in future studies of the site.

4.1.2 Height Aspects

This section discusses the results for bark samples collected from different heights of a single tree, to investigate the vertical distribution of airborne particles. For this purpose bark samples were taken from a Scots pine tree, indicated as Tree X, which was located within 10 m north of the SSD and 30 m of the MWD. Hence, the south-southeast (S-SE) side of tree X is facing both dumpsites while the NW side faces a forested area. Bark samples were collected at six different heights of 0.5 m, 1.0 m, 2.0 m, 3.0 m, 4.0 m and 5.0 m above the ground, on both the NW and SE sides. Samples of needles, twigs and cones were also collected at 5 m and 7 m height. The results for these samples are illustrated in Figure 4.4 for the tree bark and in Figure 4.6 for needles, twigs and cones.

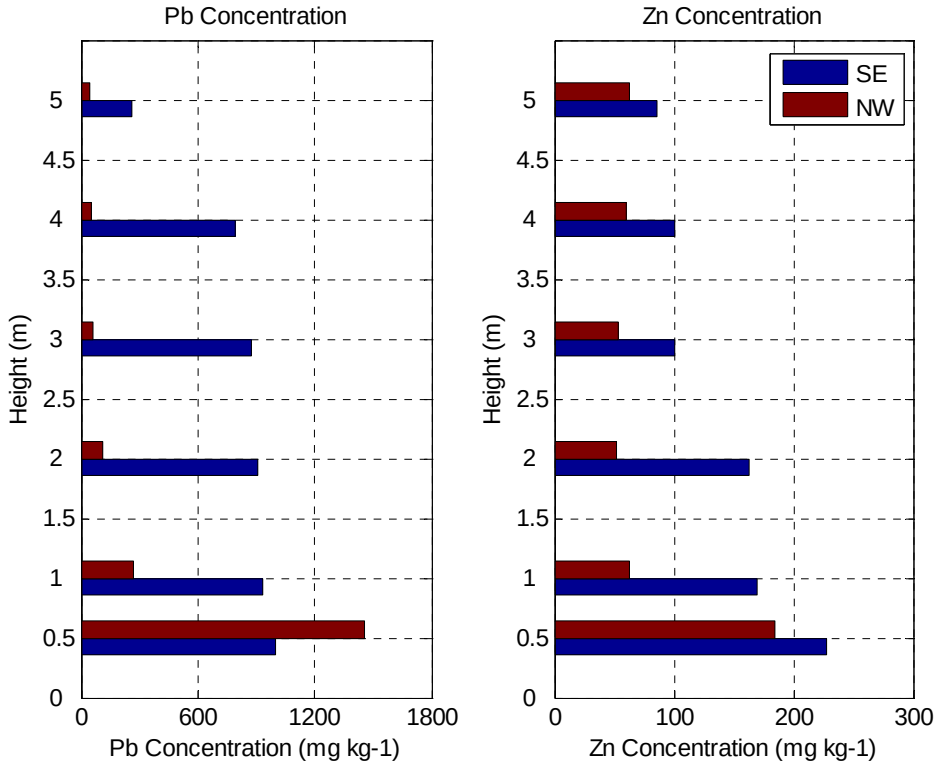


Figure 4.4: Pb and Zn Concentration in bark of tree X at Different Heights

As shown in Figure 4.4, the Pb distribution as a function of height is observed for both the SE and NW sides of the tree. Concentrations of Pb decrease, with increasing height and were, in most cases, higher in samples from the SE side of the tree. This supports the conclusion that the side facing the MWD and SSD will systematically have higher concentrations of contaminant metals. Only at the height of 0.5 m was the Pb concentration higher in the sample from the NW side. On the SE side of the tree, there is only a gradual decrease in Pb concentration with increasing height up to 4 m, within an approximate range of 1000 – 800 mg kg^{-1}. Above 4 m, there is a sharp drop in concentration from 800 mg kg^{-1} at 4 m to 300 mg kg^{-1} at 5 m. In contrast, the NW side shows a sharp decrease of almost six-fold in Pb concentration, from a maximum of approximately 1500 mg kg^{-1} at 0.5 m to 250 mg kg^{-1} at 1 m. A gradual decrease in concentration with increasing height is then observed for the rest of the samples within a range of 250 – 50 mg kg^{-1}.

The results for Zn concentrations at different heights (Figure 4.4) show systematically higher concentrations of Zn in samples from the SE side than from the NW side. The Zn concentration in samples from the SE side shows a regular decrease as the height increases, within the range of 225 to 90 mg kg^{-1}. On the other hand, the NW side shows the Zn contaminant distributed almost evenly throughout the height range of 1 to 5 m of the tree, with a range of only 52 to 63 mg kg^{-1}. The concentration at 0.5 m was however almost three-fold higher compared to the rest of the samples on the NW, with a concentration of 184 mg kg^{-1}.

The results from this section show that concentrations of both Pb and Zn decrease with increasing height, but with different patterns in their vertical distributions. One possible explanation for the decrease in concentration with increasing height could be due to the gravitational settling effects on windborne particles. Another theory is that these vertical distribution patterns could be caused by surface run-off during periods of rain. For example as Schulz et al. (1999) reported, wet and dry deposition running down the tree trunk as stem flow. Particles deposited on the bark surface could be washed off and transported downward, with partial re-deposition resulting in higher concentrations at lower heights.

The concentrations of Pb and Zn at 0.5 m height were also observed to be markedly higher than those for the rest of the tree and this affected both the NW and SE sides. This supports the suggestion by Bohm et al. (1998); Tye et al. (2006); Wolterbeek & Bode (1995) that soil particles may splash onto the trunk and influence concentrations of contaminant metals at lower heights of a tree. These results therefore support the sampling strategy employed in this research, which was based on the premise that the suitable height to collect bark samples is 1.5m. Figure 4.5 depicts the Pb/Zn ratio of the contaminants collected at different heights of Tree X. The results show varied pattern of distribution on the two different sides.

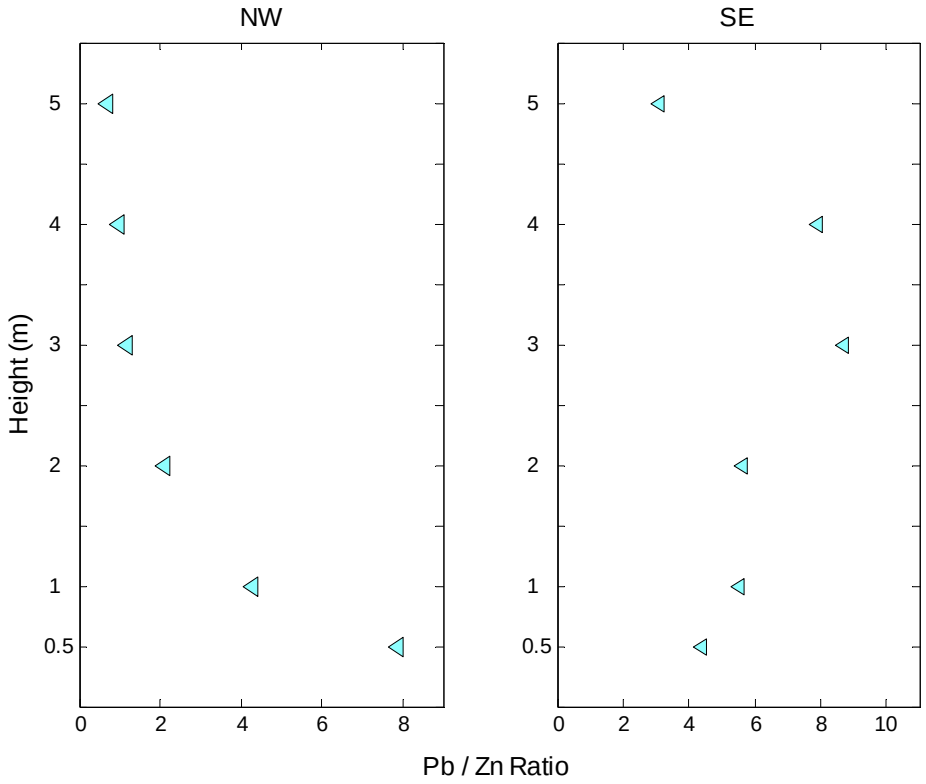


Figure 4.5: Pb/Zn Ratio at different heights and sides of Tree X

The Pb/Zn ratio on the NW side of tree X displays an exponential reduction with increased height. Within the 0.5 - 1 m height, the Pb/Zn ratio displays similar levels as that observed for previous trees located in area A. At the height of 2 m upwards, the Pb/Zn ratio reduces drastically to less than 1 at 5 m height. This could be inconsistent with the earlier suggestion of preferential leaching and downwash of Zn. The SE side on the other hand displays a high Pb/Zn ratio of 4 – 6 at the lower heights. Above 2 m however, the Pb/Zn ratio continues to show high Pb enrichment, similarly displayed for previous samples from area A.

The SE side therefore shows an uneven pattern of Pb/Zn ratio distribution, according to its height. The NW side however shows a gradual decrease of Pb/Zn ratio with increased height. Apart from analysing samples of tree bark from different heights, additional samples of needles, cone and twigs from Tree X were also taken from heights of 5m and 7 m. The results for these samples are depicted in Figure 4.6.

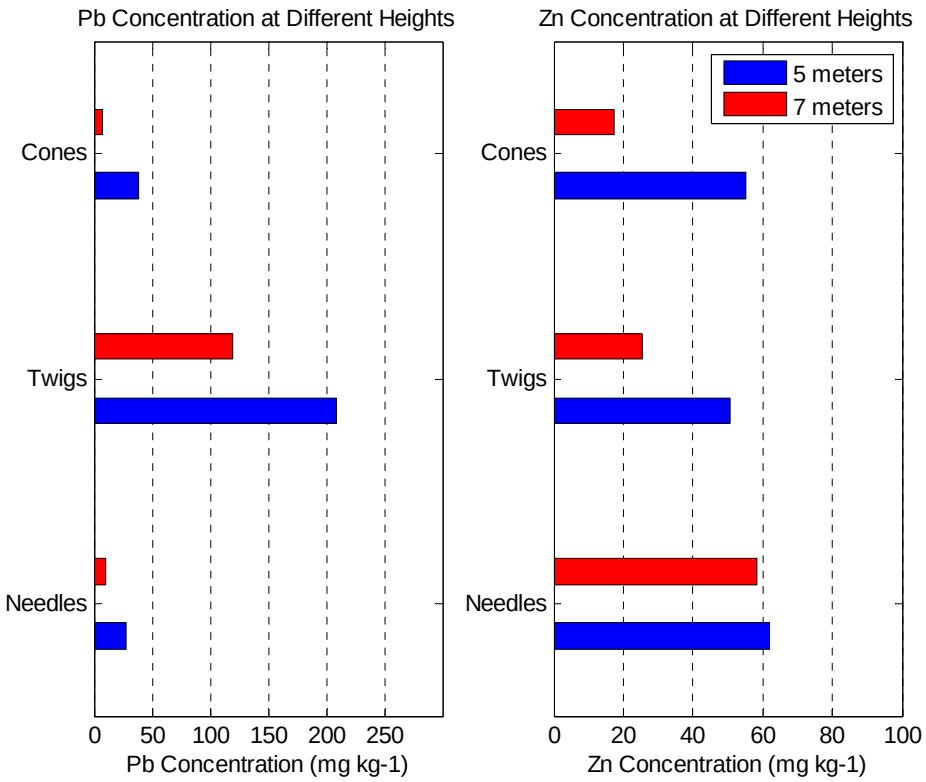


Figure 4.6: Pb and Zn Concentration in Needles, Twigs and Cones from tree X at heights of 5 m and 7 m.

Pb concentrations in the needles, twigs and cones were higher at 5 m than at 7 m for all the three sample types, with the twig samples showing a difference of almost 100 mg kg^{-1} between the two heights. The needles and cones although showing smaller differences, nevertheless demonstrate that the Pb concentration reduces with increased height. An interesting point is that the Pb concentrations for the twig samples for both heights are significantly higher than needles or cones from the same height and similar to Pb concentration on bark. Michopoulos et al. (2005) made comparisons of needles, trunk bark and trunk wood and found the average Pb concentration to be in the order of bark > needles > wood. However, the wood and bark refers to core tissues and not surfaces.

Nevertheless, in this study the average Pb concentration on both sides of tree X showed the order to be bark and twigs > cones > needles. Rademacher et al. (1986) reported that the mean content of needles was 5.5 mg kg^{-1} Pb, based on a large number of pine trees of various ages. The Pb in needles from this study shows higher concentration (10 – 28 mg kg^{-1}) probably reflecting the influence of mine waste deposition.

The Zn distribution shows a similar pattern to that observed for Pb distribution, with the concentration in each sample type decreasing as the height increase. This effect is being most pronounced for cones where a difference of almost 40 mg kg^{-1} was observed between the two heights. There was little variation in Zn concentration between samples of twigs, needles and cones at a height of 5m. However, at the height of 7 m, the Zn concentration was highest in needles and lowest in cones.

The results from this section support the earlier findings derived from bark samples between different heights in that both Pb and Zn decrease with increased heights. The aerial dispersal of Pb and Zn and its eventual attachment of these metals to surfaces of different part of a tree such as bark, needles, cones and twigs, decrease with increased height. The assumption that the low concentration of contaminant found on bark surfaces at higher parts of the tree is due to the contaminant being distributed on the needles, smaller branches, twigs and cones can also be ruled out. This is because the concentration on the samples of needles, twigs and cones were also found to decrease at increase height. This verifies the fact that the dispersal of airborne contaminants is indeed more concentrated at lower heights.

4.1.3 Age Aspects

The final section of the tree bark analysis compares the tree bark of different planting years and different species. Tree 12 and Tree X were both planted in 1891 and are from the Scots pine species. The difference between the two trees is that Tree X is situated within area A and Tree 12 within area B. Both trees are compared against Tree Y, a Sitka spruce planted in 1975.

Tree 12 and tree Y are similar in that both are located towards the far east of the mine site within approximately 50 m of each other (refer to Figure 3.11 of tree sampling map). The Pb and Zn concentrations for bark samples collected from each tree on both the SE and NW sides. The results are shown in Figure 4.7.

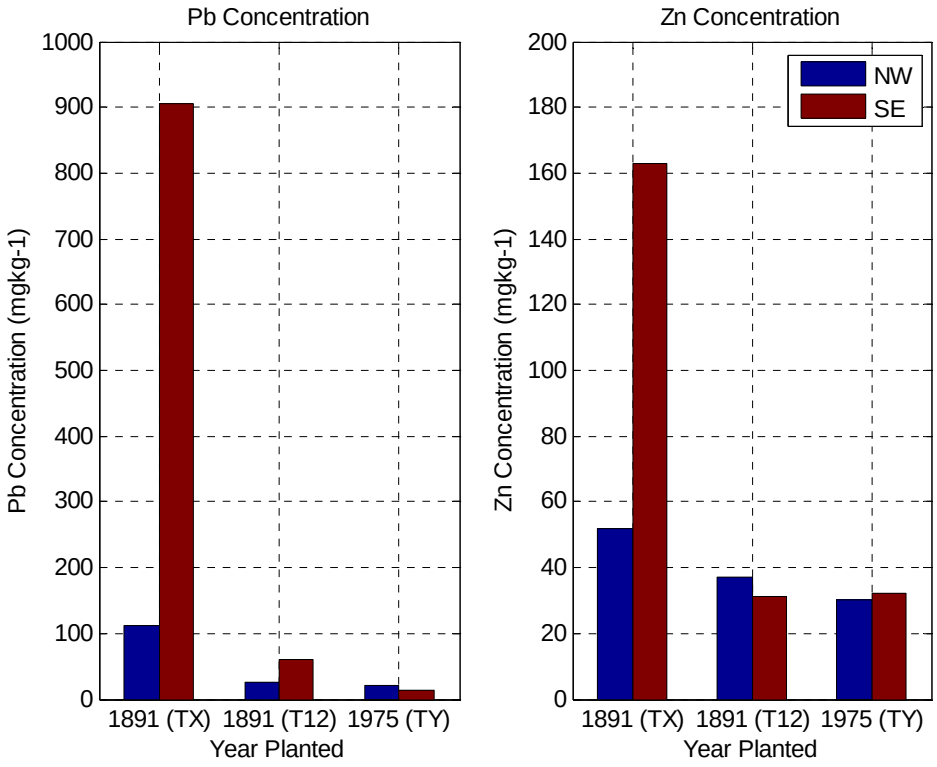


Figure 4.7: Pb and Zn Concentration in bark samples from 1.5 m height in trees of Different Age and Species (TX and T12, Scots pine; TY Sitka spruce)

Tree X displays higher concentrations of both Pb and Zn than Trees 12 and Y. This supports the earlier findings that trees closer to the source of contamination are exposed to higher concentrations of airborne contaminants than trees situated at a greater distance. As explained earlier Tree X is within area A close to the SSD and MWD, whereas trees 12 and Y are situated within a dense forest stand further east of the main area of the former mine. Trees 12 and Y in fact show very similar concentrations, especially in samples from the NW sides of the trees.

The similar distribution of contaminants for Trees 12 and Y indicates that the bark surfaces have been subjected to similar levels of airborne contaminant exposure. However, the trees are of different ages and it might be anticipated that the older Trees, 12 and X, might contain higher levels of contaminant on their bark because the bark of an older tree may have been accumulating deposition of atmospheric contaminants over a longer time. However, the results indicate that the concentrations of metals in the bark of the Scots pine species do not reflect lifetime accumulation.

According to Schulz et al. (1999) the deposition characteristics of pine stands include the aspect of the shedding process of the pine bark. In approximately 2 years, a new layer replaces the external bark. The sheets are formed growing from inside of the bark approximately 1 – 2 mm in thickness. New accumulation process will start after each renewal of the external bark layer. Thus, airborne deposition on bark surfaces of pine trees will contain similar levels of concentration regardless of age.

Hence, the results from this section give evidence that the metals found on these bark samples are of contemporary origin. This supports the speculation that the contaminants from the dumpsites are still actively dispersed through the atmosphere within the surrounding area of the former mine. It also strengthens the results from previous sections that bark surfaces are subjected to higher contaminant levels based on distance from the former mine's dumpsites.

4.1.4 Summary

The overall results from the tree bark analyses have given an insight into the airborne deposition of Pb and Zn within the former mine. The most intense contamination was found contained within about 50 m distance from the waste dumpsites. Beyond this distance, the concentrations were found to be significantly lower. Different sides of trees also showed prominent differences closer to the point source than further away. It is thus suggested that atmospheric dispersal of the contaminants from the site is largely localised and reduces with distance.

The concentrations of Pb and Zn were also found to generally decrease with increased height. This was supported from similar evidence found on needles, twigs and cones. This study has also found similar levels of concentration on bark of different ages and species. It can be concluded that due to the shedding process of bark, the concentration measured on the tree bark reflects recent deposition. This indicates that contaminants within the site are still continuously being distributed via aerial dispersal.

In addition to that, the study also exhibits the significance and importance of height and facing aspects of tree bark during sampling. The different trends of dispersal found when comparing both aspects displays the importance of a systematic approach when using bark as a tool for atmospheric dispersal studies. The study also supports the use of Scots pine species as suitable indicators of airborne dispersion.

The first section of the study has given valuable information on atmospheric dispersal within the site. The tree bark results however represented aerial deposition only on the northwest side of the mine site where the forested area is located. The study continues to investigate atmospheric dispersal on the northeast side using peat cores samples.

4.2 Peat Cores

This section presents the results for the analyses of peat core samples. Cores 1-4 were collected at the main mine site and Cores 5-8 were collected further north of the mine site. Therefore, the results will be explained accordingly in two separate sub-sections.

4.2.1 Peat Cores 1- 4

Cores 1-4 were collected at the small side dump (SSD) at the main mine site at Tyndrum, which has an area of about 100 m^2. The sampling location of each core is as illustrated in Figure 3.9. The cores were collected between 5 cm – 10 cm where the depths of peat overlying mineral soil for Cores 2 - 4 were found to be restricted to 3 – 4 cm layers. Core 1, which was collected further south from the SSD contained organic material reaching 8 cm in depth.

In addition to measuring Pb and Zn concentrations in 1 cm vertical increments of the samples, the accumulation rate for Cores 1 and 2 was also established using the ^{210}Pb dating method. As explained in Section 2.2.1, the Constant Initial Concentration (CIC) model was used to calculate the age of the samples from each depth within the profile. The Pb and Zn concentration profiles are plotted in Figure 4.8 and Figure 4.9 respectively. The Pb/Zn ratio was also presented as shown in Figure 4.10 and the ^{210}Pb dating results are depicted in Figure 4.11.

As shown in Figure 4.8, Pb concentrations for Cores 1-4 ranged between 50 mg kg^{-1} and 5000 mg kg^{-1}. The overall trends revealed a general similarity between the four core profiles, with all showing a marked peak in concentration at about 6 – 7 cm.

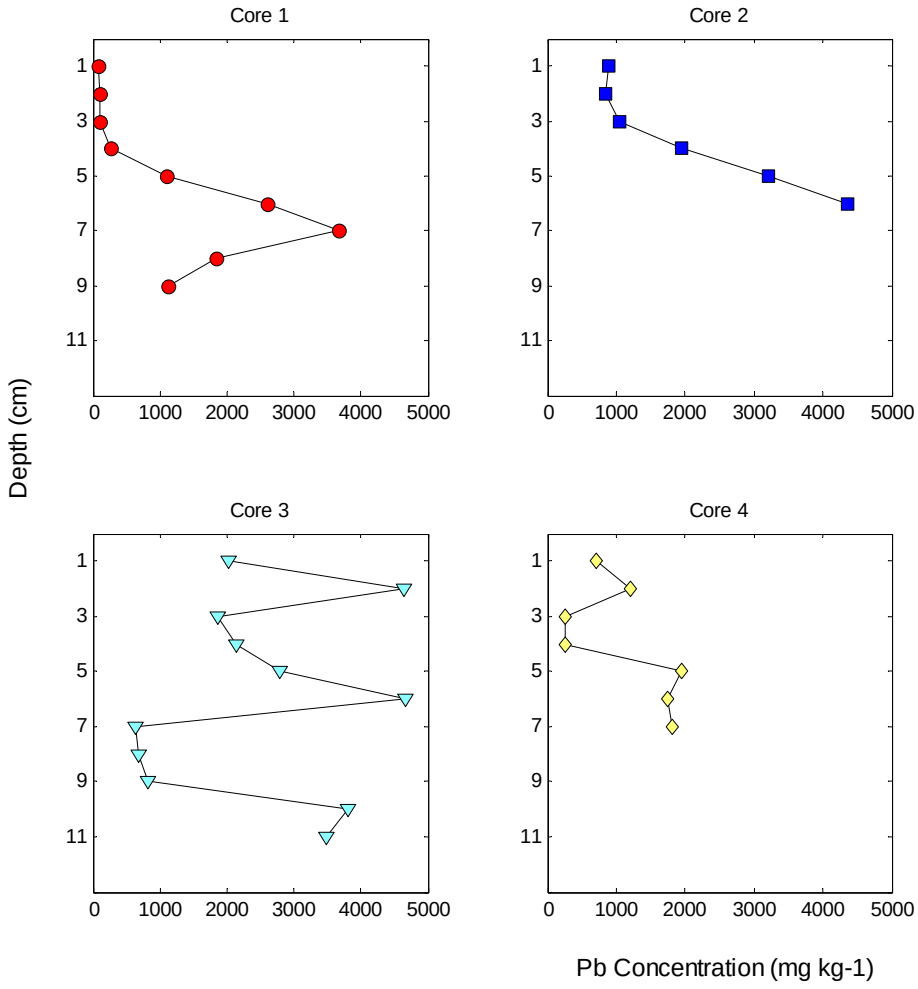


Figure 4.8: Pb concentration profiles for peat cores 1-4

From the surface to 2 cm depth, Cores 1 and 2 show almost constant concentrations, below which there is a continuous increase to reach peaks at 6 cm – 7 cm. Core 1 subsequently shows a steady decrease in Pb concentration below this depth towards the base of the core. Core 3 reveals a marked increase in concentration below 3 cm depth, with a peak of approximately 5000 mg kg^{-1} at 7 cm. Resembling Core 1, the Pb concentration in Core 3 then decreases to a minimum at 8 cm – 9 cm, below which it increases again. Core 3 shows a complex profile with minima at 4 cm and 6 cm and maxima at 2, 7 and 10 cm. Core 4 reveals a decrease in Pb concentration from the surface to a relatively constant value between 1 – 2 cm depth below which the concentration increases to the base of the core.

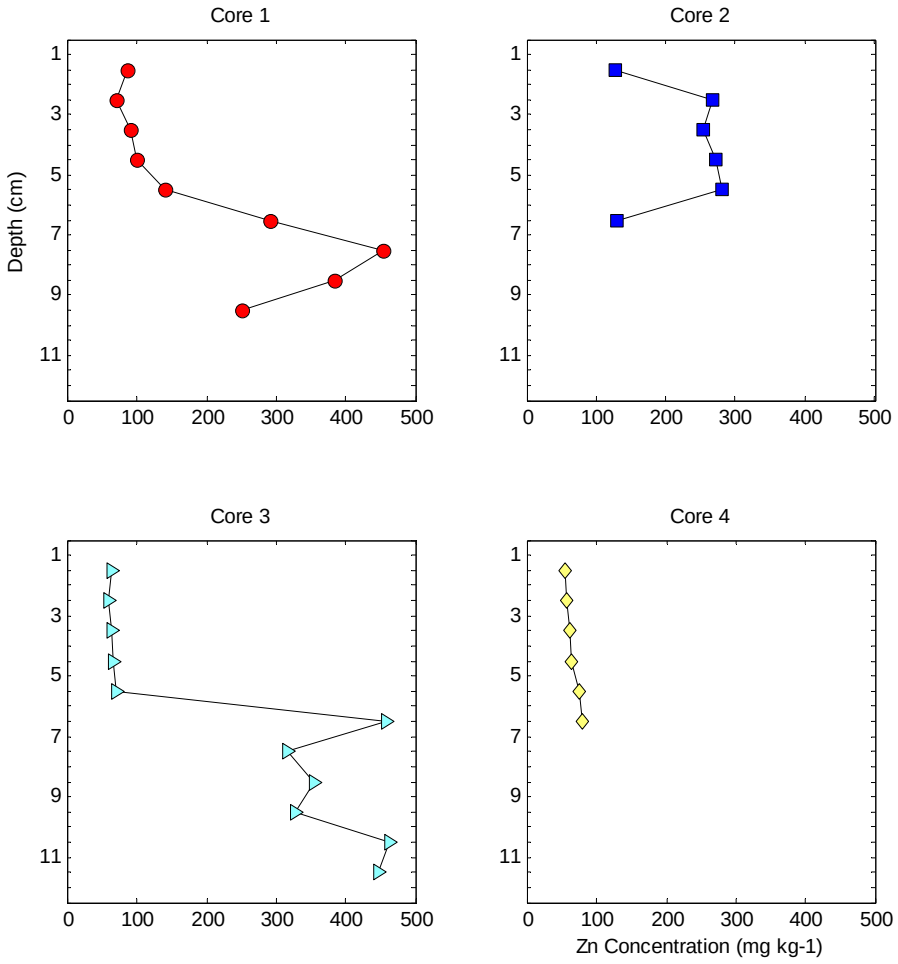


Figure 4.9: Zn concentration profiles for peat Cores 1-4

The Zn concentration profiles for Cores 1-4 are shown in Figure 4.9. The concentration range was found to be between 50 mg kg^{-1} and 500 mg kg^{-1}. Except for Core 2, all of the other cores show only small variations in concentration within 4 cm of the surface. A sharp increase then follows below this depth, with Cores 1 and 3 reaching similar peak values of an almost 500 $mgkg^{-1}$ at 6 cm – 7 cm depth. Concentrations in both cores then decrease towards the base, but with Core 3 displaying another peak at 10 cm depth. With a length of only about 6 cm, Core 4 showed a steady concentration throughout the profile with no apparent peak, while Core 2 showed two peaks of similar values at the surface and at 6 cm depth.

The Pb/Zn ratio was also plotted for Cores 1 - 4, as shown in Figure 4.10. Core 1 and Core 2 display Pb/Zn ratios of 1 – 15 although they show different trends. Core 1 has ratios of below 5 within the top 4 cm where it shows a slight increase between 6 – 8 cm. Core 2 on the other hand has higher ratios at surface level, below which the ratio gradually reduces down to the core.

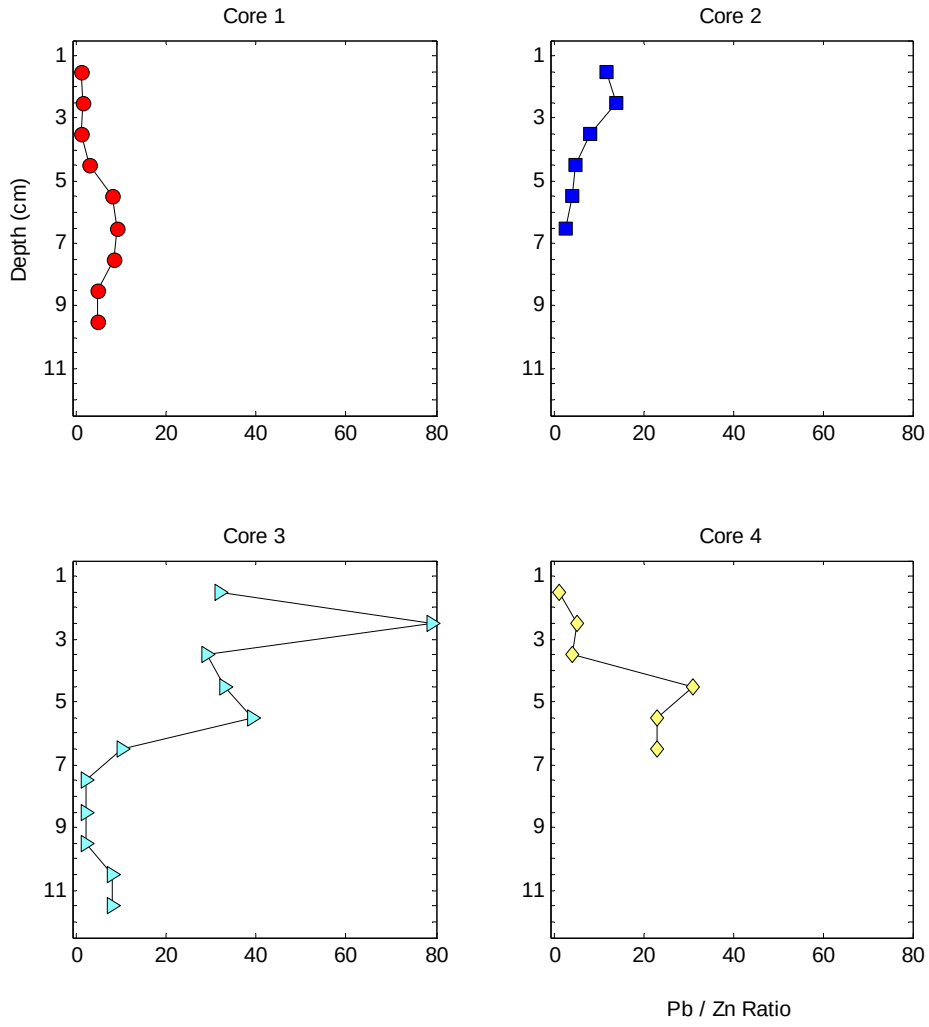


Figure 4.10: Pb/Zn ratio for Cores 1 – 4

Core 3 displays an irregular trend at the top layers with a high Pb/Zn ratio of ~ 80 at 2 cm depth. The ratio then reduces before which it displays another slight increase at depth of 4 – 6 cm before reducing towards the core.

Core 4 meanwhile, shows a gradual enrichment in Pb with increasing depth with Pb/Zn ratio of below 10 within the first 3 layers and reaching a ratio of 31 at 4 cm below which the ratio reduces to a value of 23 for its lower depths.

The ^{210}Pb chronologies for cores 1 and 2 are shown along with the Pb concentration profiles in Figure 4.11. Higher Pb and Zn concentrations at depth provide evidence of higher levels of deposition in the past.

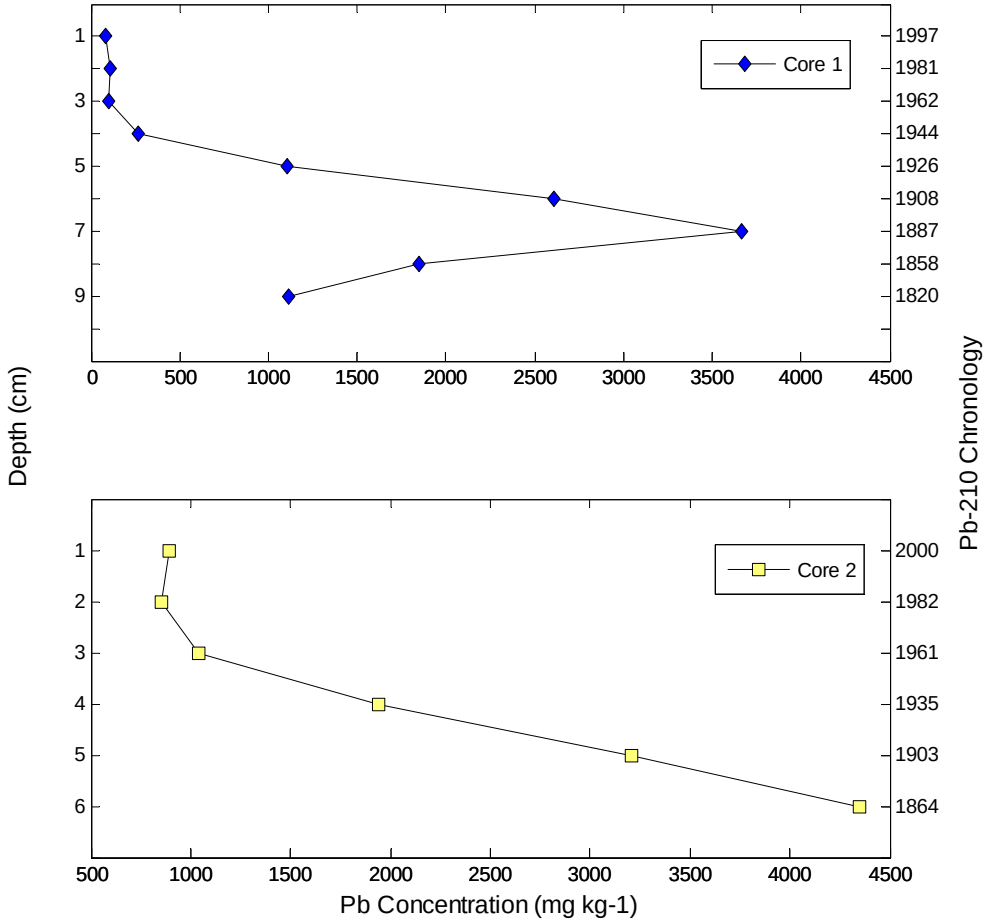


Figure 4.11: ^{210}Pb-dating on Cores 1 and 2

The ^{210}Pb chronologies indicate that the peak Pb concentrations for cores 1 and 2 at 6 cm – 7 cm depth was dated between 1864 to 1887. This timescale is consistent with deposition of material containing high Pb levels during the period when mining activity at Tyndrum was active.

Wilson (1921) and Pattrick (1985) reported that the waste dumps in Tyndrum were reworked during 1916 – 1925 and evidence of this reworking has been observed in peat cores from locations closer to the reprocessing site (MacKenzie and Pulford 2002). However, the input of high concentrations of Pb to cores 1 and 2 in the present study clearly occurred before the waste reprocessing took place. Thus, the peak could probably imply the period when the small side dump (SSD) was formed. This might also indicate direct rather than windborne deposition of the Pb in the soil at the time.

4.2.2 Peat Cores 5- 8

Cores 5-8 were collected at an area north of the main site as shown in Figure 3.10. The concentration results for the cores are depicted in Figure 4.12 and Figure 4.13 for Pb and Zn, respectively. The Pb/Zn ratio is also included as shown in Figure 4.14. The ^{210}Pb dating technique was used to obtain the accumulation rate for core 7. The age of samples from the profile was then determined as displayed in Figure 4.15.

The results reveal a large difference in Pb concentration range from each of the cores with, for example, Core 7 having concentrations below 300 mg kg^{-1} whereas Core 8 has a peak concentration of 1500 mg kg^{-1}. Both of these cores display maximum concentrations at, or near, the surface, with a decrease in concentration with depth. Core 7 showed a constant decrease towards the base of the core to a value of 0.7 mg kg^{-1} at the base of the core, which may represent the background levels of Pb for peat in this area. In addition to the peak at 2 cm, Core 8 also showed a smaller peak at 6 cm, reaching 500 mg kg^{-1}, below which the concentration decreased to the base of the core. Unlike Cores 7 and 8, Cores 5 and 6 reveal a contrasting trend of increasing Pb concentration with increasing depth.

Both cores had concentrations of approximately 50 mg kg^{-1} of Pb at the surface, with a systematic increase in concentration towards the bottom of the core, interrupted in core 5 with a subsurface peak at 4 cm. Core 5 reached a maximum concentration of approximately 700 mg kg^{-1} at 10 cm depth, while Core 6 exhibited a maximum of about 1300 $mgkg^{-1}$ at the same depth. This similarity in distribution of Pb is reasonable, given the closely spaced sampling location for Cores 5 and 6.

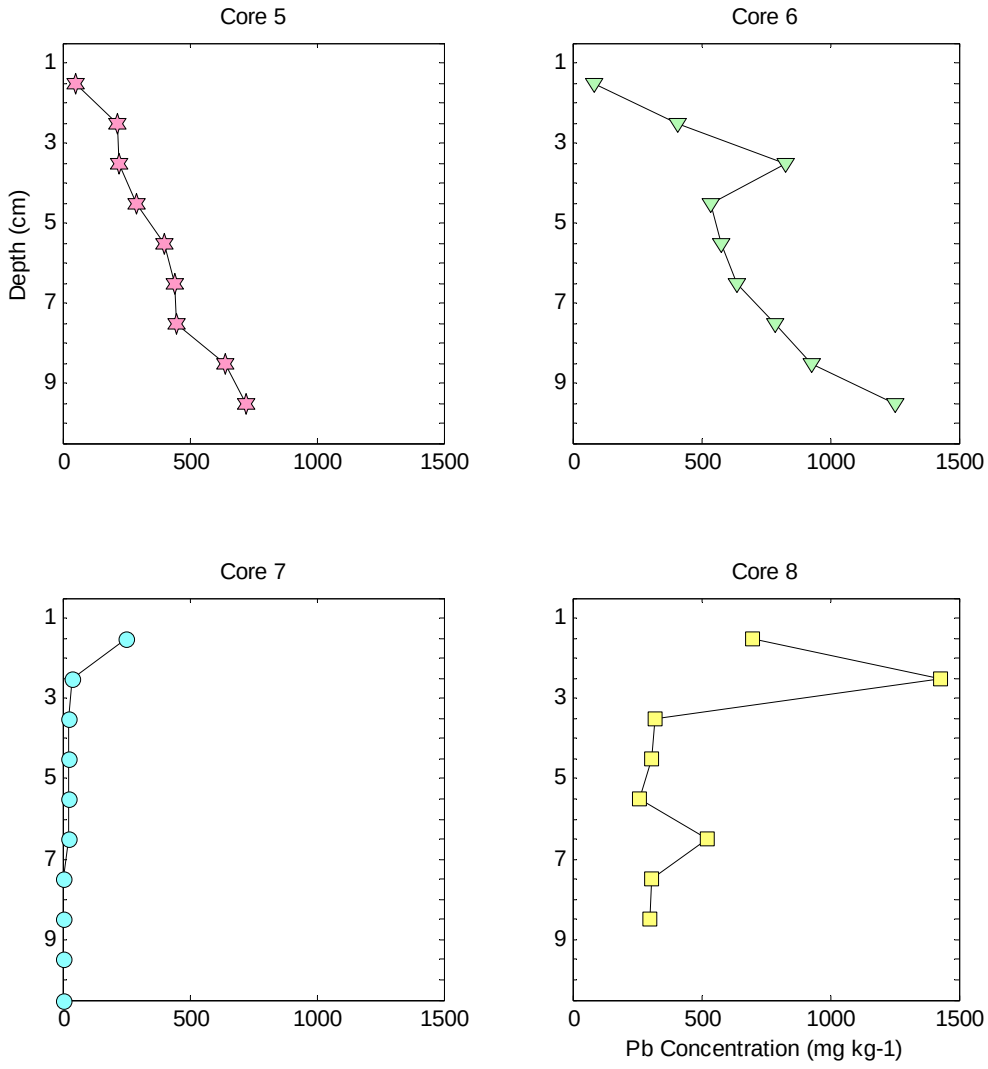


Figure 4.12: Pb concentration profiles for peat Cores 5-8

The Zn results for cores 5 – 8, shown in Figure 4.13 display similar concentration ranges for cores 5, 6 and 7 from approximately 50 mg kg^{-1} to 150 mg kg^{-1}. Core 8 has a much higher range of between approximately 200 mg kg^{-1} – 400 mg kg^{-1}. The surface sample showed the highest concentration for core 8, below which values decreased steeply to ~ 220 – 250 mg kg^{-1} from 2 – 4 cm depth.

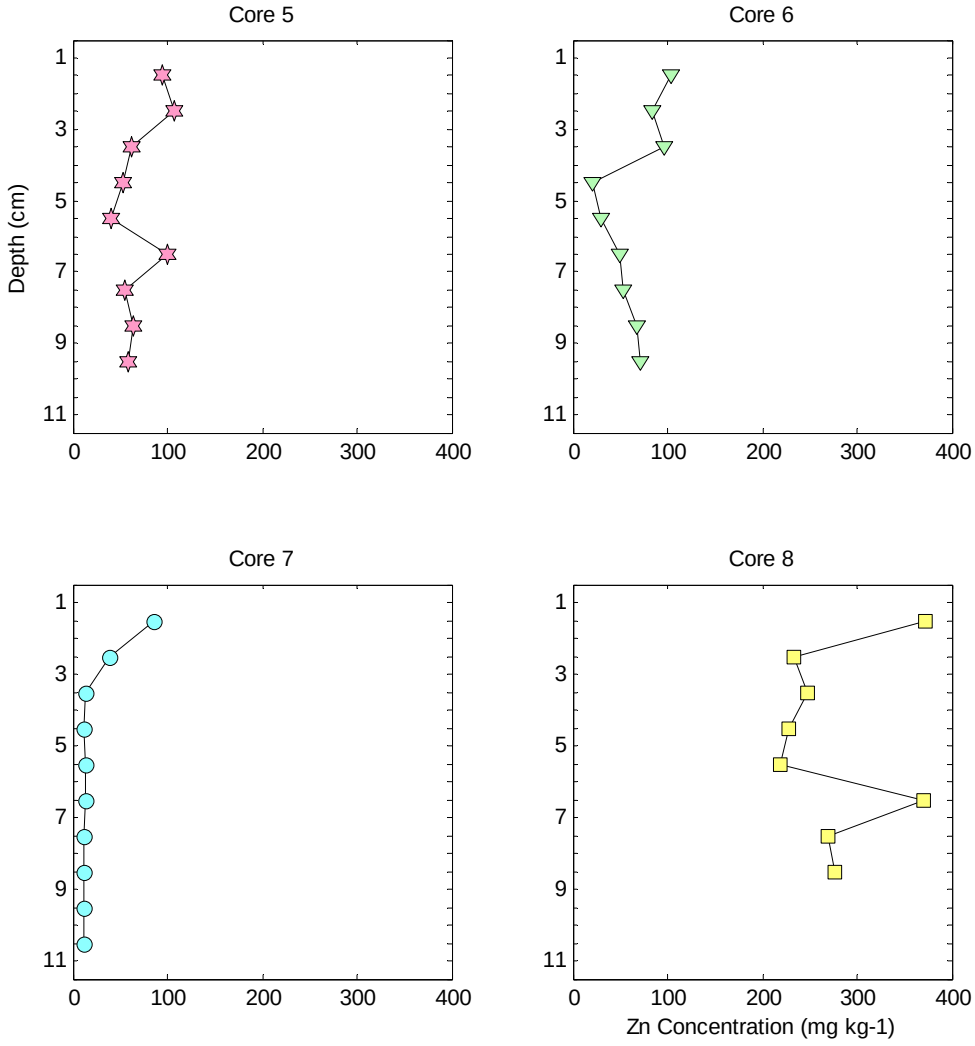


Figure 4.13: Zn concentration for Cores 5-8

The concentration profile then exhibited a peak of ~ 400 mg kg^{-1} at 6 cm depth below which it decreased to the bottom of the core. Cores 5 and 6 exhibited irregular variations throughout the profile. In contrast, Core 7 exhibited maximum Zn concentration in its surface soil, with a systematic decrease with increasing depth, similar to the Pb concentration profile. The Pb/Zn ratio for core 5-8 was also plotted as shown in Figure 4.14.

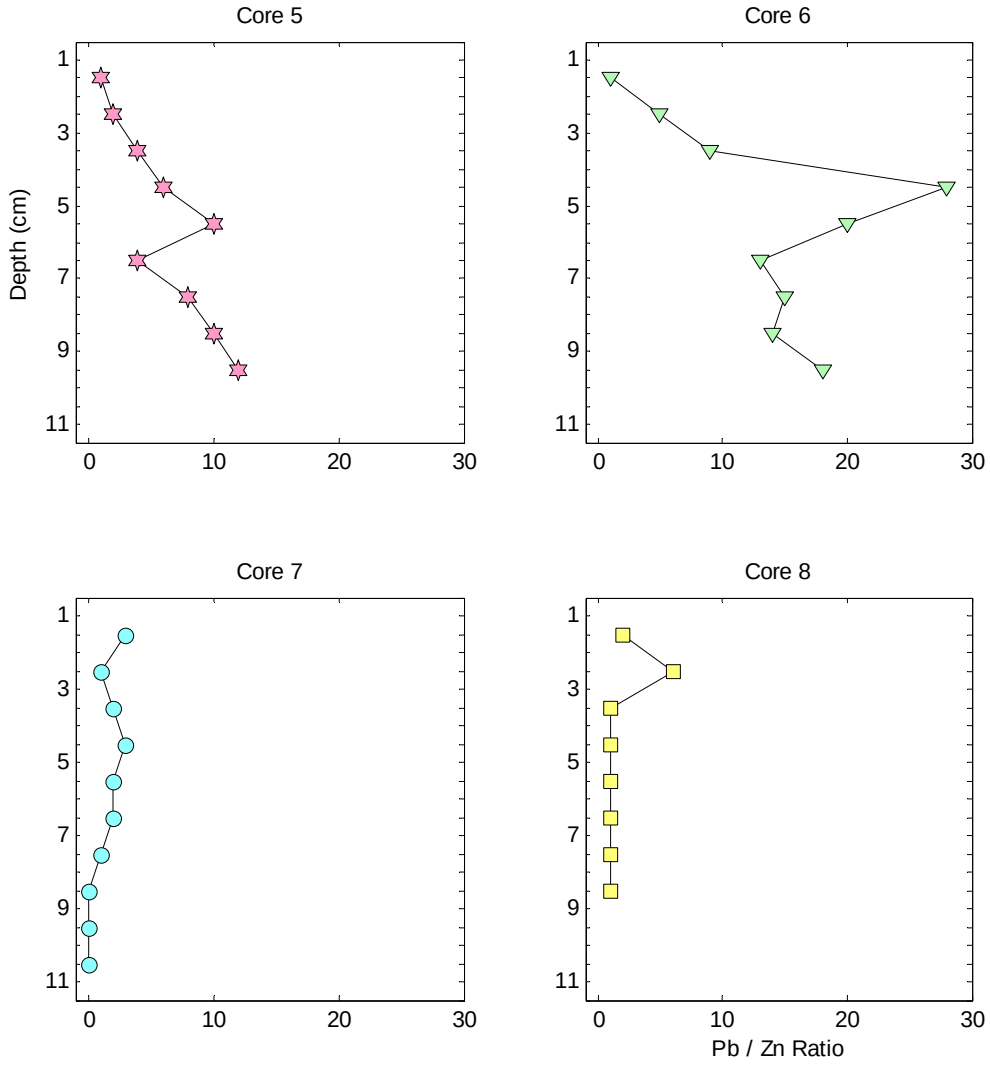


Figure 4.14: Pb/Zn Ratio for Cores 5 – 8

Cores 5 and 6 show similar trends of increased Pb/Zn ratio with increased depth with a decrease at 6 cm, below which the ratio increases again. However, both cores reveal different ranges, with core 5 having Pb/Zn ratios of 1-12 while core 6 with higher ratios of 1-28. Cores 7 and 8 reveal similar trends of Pb/Zn ratio, which decrease towards the base of the core. The average Pb/Zn ratio for core 7 and 8 are 1 and 2 respectively.

As mentioned previously ^{210}Pb dating was also carried out for core 7. Figure 4.15 shows the ^{210}Pb chronology for core 7 along with the Pb concentration profile.

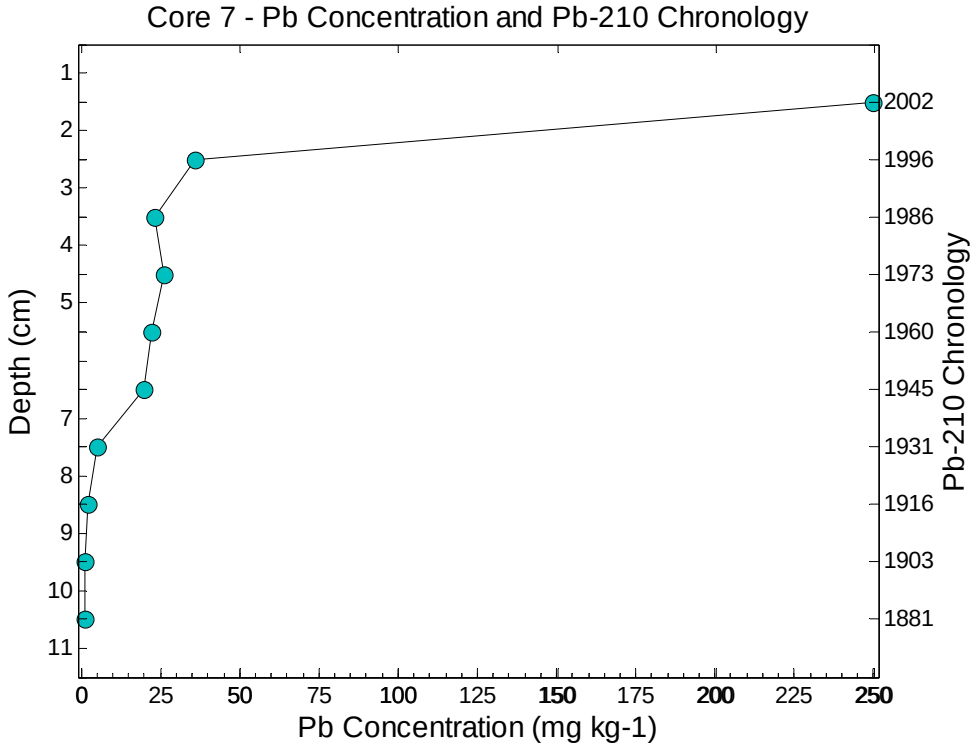


Figure 4.15: Pb concentration profile and ^{210}Pb chronology for Core 7

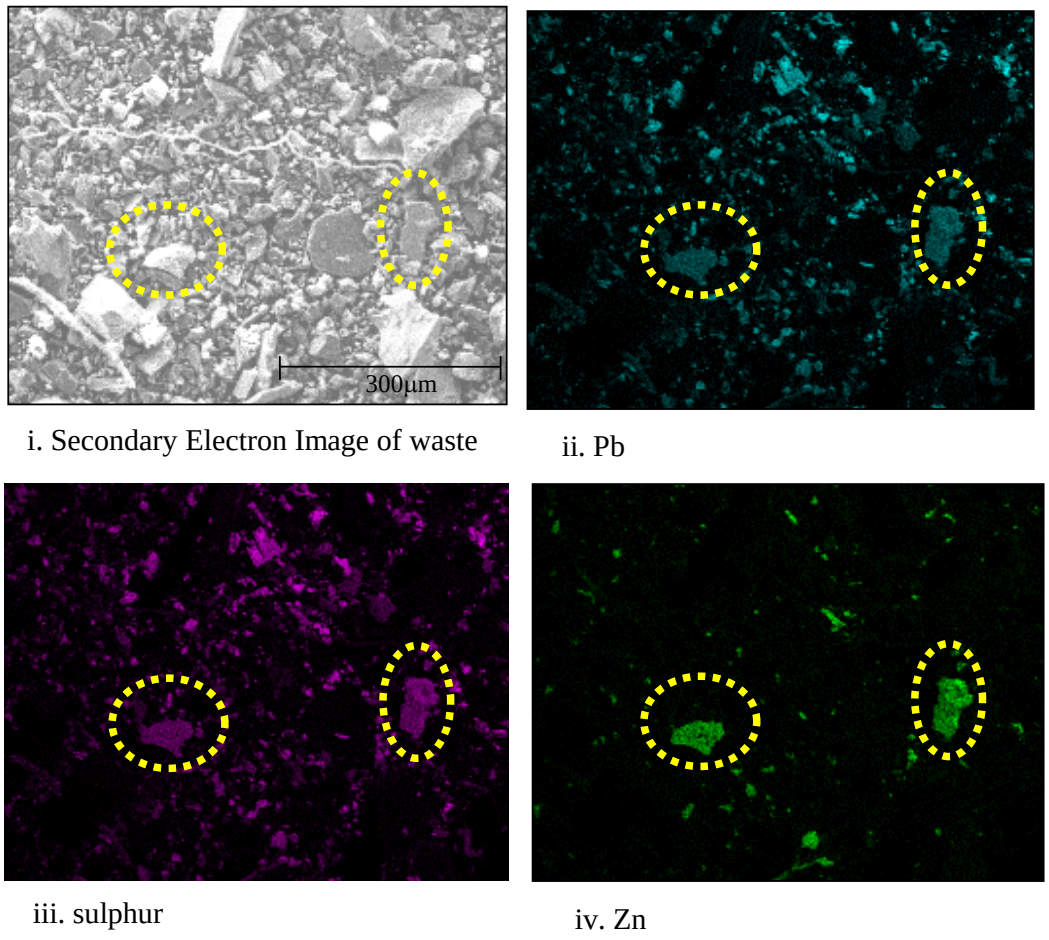
The results reveal that the high Pb concentration found in the upper soil layers were deposited within the past 6 years. Prior to this period, the core did not display any substantial peaks or high levels of Pb deposition. Based on this it could be suggested that the Pb deposition within the area is of contemporary source. This supports the tree bark study that reflects recent atmospheric deposition.

The chronology results also reveal the possibility that the Pb could have originated from the main mine due to possible re-distribution process of the former dumpsites. Although the surface concentrations compared to that measured in cores 1-4 are lower this might be due to the distance of core 7 from the main mine. Another possible suggestion is that the Pb might have originated from sources other than the mine. This is because the profile does not seem to show any evidence of past deposition even at the time mining was active. Based on the chronological results of core 1 and 2, this should have been apparent within the 10 - 11 cm depth of core 7, which refers to the late 19th century. Thus, the recent Pb deposition may reflect influence from other possible nearby sources.

4.2.3 Scanning Electron Microscope (SEM)

Images of mine waste from the dumpsite and a sample of peat from Core 8 (from layer with high Pb content) were compared using a scanning electron microscope (SEM). The SEM creates images using high energy beams of electrons onto the the surfaces of samples and receives various types of signals such as secondary electrons, characeristics x-rays and back scatter electrons. These signals are then used to recognise and detect the elemental composition of a particular sample. The principles of the SEM are explained in Section 3.3: Methodology of Laboratory Analysis.

Figure 4.16 shows the first set of SEM images of samples collected from the Tyndrum waste dump. The high-resolution images are under 400x magnification and reveal the three-dimensional appearance of the surface structure of the sample. The first image in grey shows the secondary electron image of the sample. The rest of the images show individual elements identified in different colours; Pb(blue), Zn (green) and sulphur (purple), based on its backscattered electrons. Upon comparison, the images were able to show the elemental composition of the waste which includes the presence of galena (lead sulphide) and sphalerite (zinc sulphide).



i. Secondary Electron Image of waste

ii. Pb

iii. sulphur

iv. Zn

Figure 4.16: SEM images of a Tyndrum waste sample showing the elemental composition of Pb, sulphur and Zn.

The SEM images of Core 8 at 5-6 cm depth are as shown in Figure 4.17 under 100x magnification. The images also reveal the presence of Pb, Zn and sulphur. One particular particle, highlighted in red in the figure shows the presence of all three of the elements whereas the particle in blue shows that it contains Pb and sulphur. These images are consistent with the Tyndrum waste images in Figure 4.16, which shows the presence of similar elements. This implies that the waste material has been transported via aerial dispersal and deposited at the location of Core 8, over 350 m towards east from the waste dump. The SEM images thus provide evidence of waste particles that have been deposited via aerial dispersal and persist in the peat.

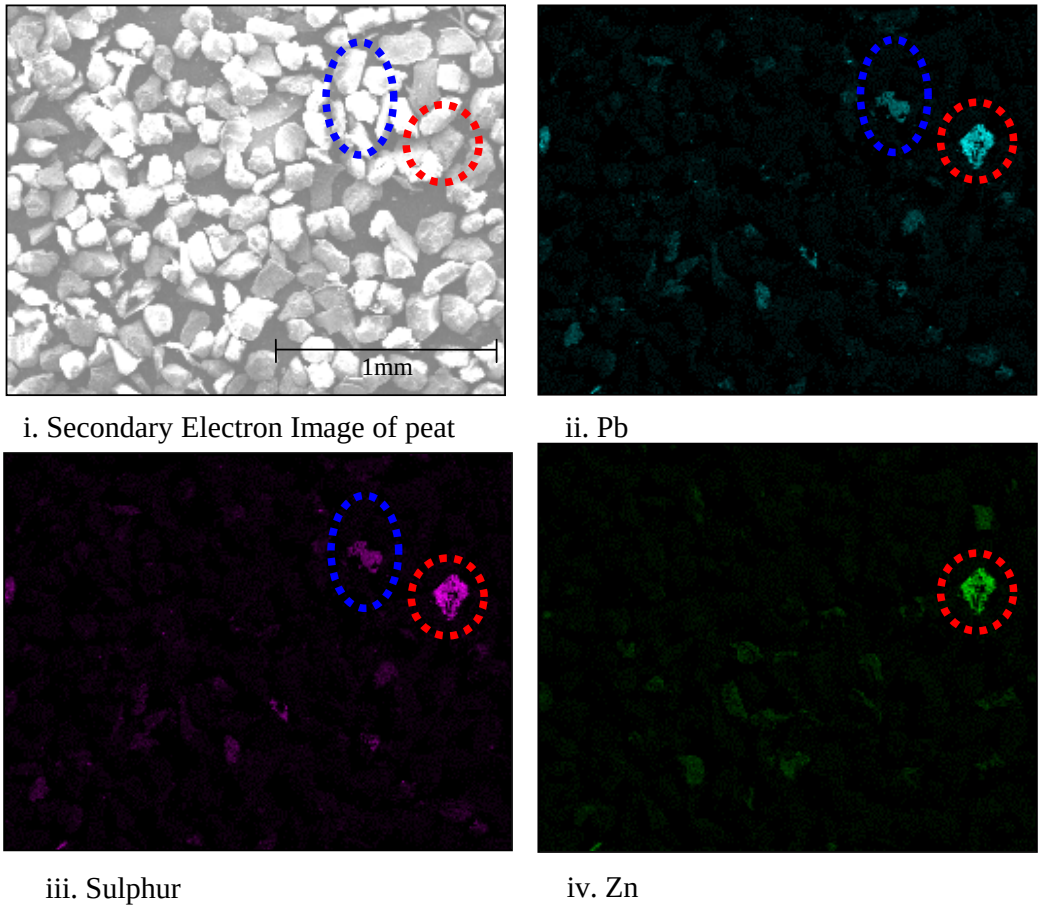


Figure 4.17: SEM images of peat Core 8 (at 5- 6cm depth) show similar composition as Tyndrum waste.

As previously discussed, the bark sample studies have shown that the waste materials are contained within 150 m of the dumpsites. It was assumed however that the dispersal of the waste might travel much further on the east side due to the lack of trees. The SEM images now give probable evidence that the waste material may have travelled and deposited within this area. The depth in which the sample was collected may also correspond to a period when the mine was active. Although a ^{210}Pb-dating method was not done in this study, it can be further verified in future studies. The SEM images have nevertheless given new evidence of the presence of materials of the waste at far distances from the main mine site.

4.3 River Water and Sediments

The river water and sediment section focuses on the investigation of heavy metal within the fluvial system. As mentioned previously, high levels of Tyndrum Pb were found in Loch Tay, 50 km away (Farmer et al. (1997a)). This section looks into the various phases by which heavy metals from the mine travel within the river system. Heavy metals in the aquatic environment are distributed among aqueous phase, suspended particles and sediments. Suspended particles are important in controlling the reactivity, transport and biological impacts of metals, while sediments play an important role as a sink and possible source of trace metals (Pertsemli & Voutsa (2007)). The investigation thus focuses on the different phases of the metals, as heavy metals exist in surface waters in dissolved, colloidal and particulate phases. The results are separated into three sections beginning with the dissolved or solution phase from the river water samples within the main mine. The second section will focus on the suspended matter or colloidal phase from river water samples outside of the mine area. The final section will look into the particulate phase or the sediments from the riverbed and riverbank sample.

4.3.1 River Water Samples

This section focuses on the results of the river water samples collected from the complex of small streams that drain the main mine site, referred to as Water 1 – 12. The samples were collected from rivers that are not necessarily continuous with each other, as shown in the sampling map in Chapter 3, Figure 3.11. As described in the sampling and methodology section, all of the samples were taken on four occasions in January, April, August and December 2005.

Figure 4.18 displays the Pb concentration in the river water samples within the main mine site. The trend is similar between the four batches throughout the twelve sites. An average concentration line is included in the graph to reveal an overall trend. The concentrations were found to be within a very small range of 0.3 – 2.0 mg l^{-1} of Pb. Nevertheless, the graph indicates a clear trend throughout the 12 locations.

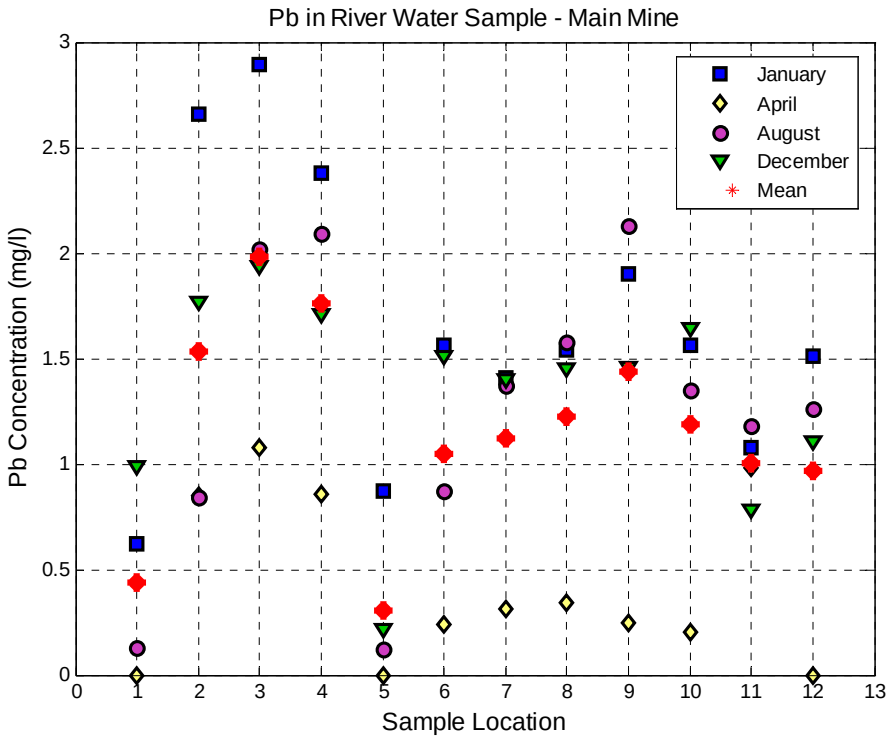


Figure 4.18: Pb concentrations in River Water from main mine site (Water 1 – 12)

Water 1, which is located to the north west of the site, shows consistently low concentration on all four occasions. This site represents the river water prior to entering the main mine site, and the low Pb concentration in water before being influenced by metals from within the former mining area. The locations that follow, Waters 2, 3 and 4, display sharp increases in Pb concentration compared to Water 1. This probably indicates the effects of the former mining as the locations of these streams are within the main mine site. Water 5 however, shows a surprisingly low Pb concentration, considering its location was just below the base of the mine. This was observed on all of the four batches collected. The rest of the river water samples, Water 6 - 12 generally show similar, relatively high concentrations compared to Water 1, indicating influence of the former mine.

The overall Pb measured in solution is very low in concentration. Due to the possibility that Pb might be transported within the river as particulate material, the water samples were filtered to physically remove any particles, and acidified to dissolve any Pb held in this form. The results obtained from both processes are displayed in the following section. The twelve river water samples that were filtered and acidified are shown in Figure 4.19. Each of the Pb concentrations displayed in the figure is the average value of four batches of samples.

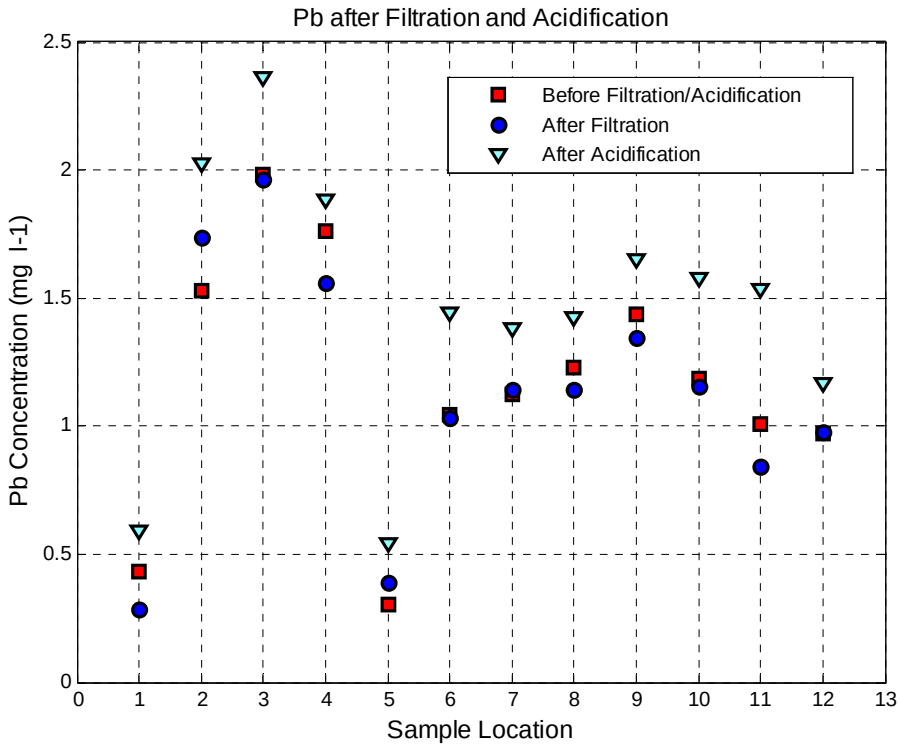


Figure 4.19: Pb Concentration after Acidification and Filtration Process

The results reveal a slight increase after the acidification process. This process was conducted in an attempt to displace Pb from any possible suspended materials that it is attached to, into the solution phase. As explained earlier, a low pH may release metal ions from its sediment site into the water column. Although the increases observed were very small, the additional Pb could possibly indicate a contribution from within the suspended solids or sediments and released into the water solution phase.

The filtration process reveals very minimal change after passing through the 1.2 µm filter. The results fail to display any significant trend that can be considered to be relevant. Based on this information, it can be assumed that the Pb concentration measured in the river water samples reflects Pb solely within its solution phase without any contribution from the > 1.2 µm size fraction that was removed.

Figure 4.20 displays Zn concentration in the twelve river samples collected from the main mine site. As observed with the Pb results, the Zn concentrations between the four batches of samples show similar trends. The figure also includes the average concentration of the four sets of results to display an overall trend. The Zn concentration has a small range of between 0.5 mg l^{-1} – 4.0 mg l^{-1}.

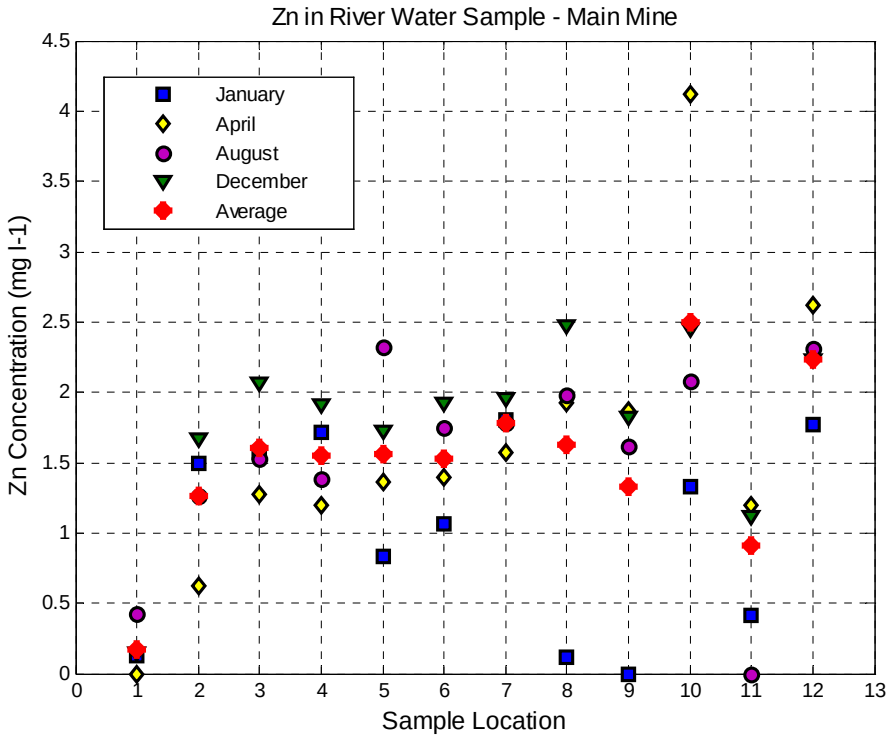


Figure 4.20: Zn Concentration in River Water from main mine site (Water 1 – 12)

The results consistently show Water 1 containing very low Zn concentration. Based on its location, the result is as expected and reveals the Zn content in the river before additional input from the mine. The rest of the samples located within the mine site reveal higher Zn in relation to Water 1. Water 2 though to Water 9 show little variation in concentration, with an average of 1.5 mg l^{-1} of Zn. The concentration then rises to a much higher value at Water 10 and 12.

The Zn concentrations after the acidification and filtration processes are as displayed in Figure 4.21. In this case, acidification did not show any consistent trend in changes of Zn concentration in solution. However, the results may reflect slight contamination of Zn from the 1.2 μm filters. This has been shown in other work carried out in this laboratory (Matoug, personal communication).

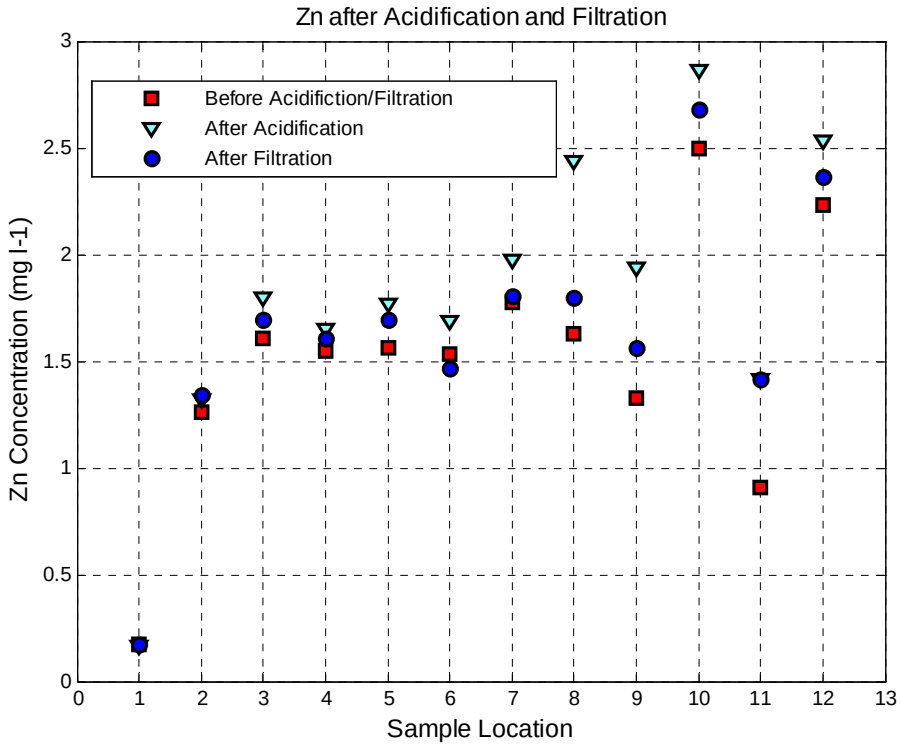


Figure 4.21: Zn after Acidification and Filtration Process

As also shown in the Pb analyses, the Zn results reveal an increase in concentration as the water passes the mine site. This gives evidence that the small rivers and streams that pass through the main mine site carry with them a certain amount of metal contamination, which is carried further downstream within the fluvial system. The presence of Pb and Zn from the main mine however were found in very low concentration within the solution phase. Consequently, the transport of contaminants within solution phase could be considered as negligible. Thus, investigation was continued on river water samples further from the mine, focusing on the presence of metal dispersal within the suspended particulate and sediment phase.

4.3.2 River Water Samples – Suspended Particles

The following sections are focused on samples collected from the fluvial system outside of Tyndrum main mine site. All of the eight water samples, Water 13 – 20 were collected during two occasions in 2006 and 2007. The locations of the samples are as shown in the sampling map in Figure 3.12. It is worth mentioning that the analyses on Pb and Zn concentration in solution were also carried out for these eight samples. However, the concentrations of both elements were found to be below the detection limit. It is observed that Water 13 – 20 involves locations of wider and larger rivers and lakes, where the concentration of metals within the solution would have been greatly diluted. This supports earlier analyses taken from smaller rivers from the main mine site, where the concentration within the solution phase was already very low.

Investigation into metal concentration was then focused on the suspended particles. Size fractions larger than 1.2 μm and between 1.2 μm – 0.2 μm were extracted by filtration and analysed for both Pb and Zn. The results for Pb concentration in the suspended materials are shown in Figure 4.22, for both batches of samples (2006 and 2007).

The Pb concentration for samples in 2007 for both size fractions however, were found to be below the detection limit of the AAS (0.3 mg l^{-1}). The larger size fraction particles (>1.2 μm) were then re-analysed using the ICP-MS. Due to its lower limit of detection (20 – 40 parts per billion) the concentration results were successfully obtained.

The metal concentration in this section is presented as mg m^{-3} as it represents the amount of metal in particulate phase in a given volume of river water. In terms of the flux of metal in the river system, this is of more concern than the metal concentrations in the particles based on units of mg kg^{-1}.

Figure 4.22 shows Water 13 - 20 plotted on the x-axis according to its approximate distance from Tyndrum main mine. All of the samples represent suspended particles collected from rivers except for Water 17 and 18, which were collected from lakes.

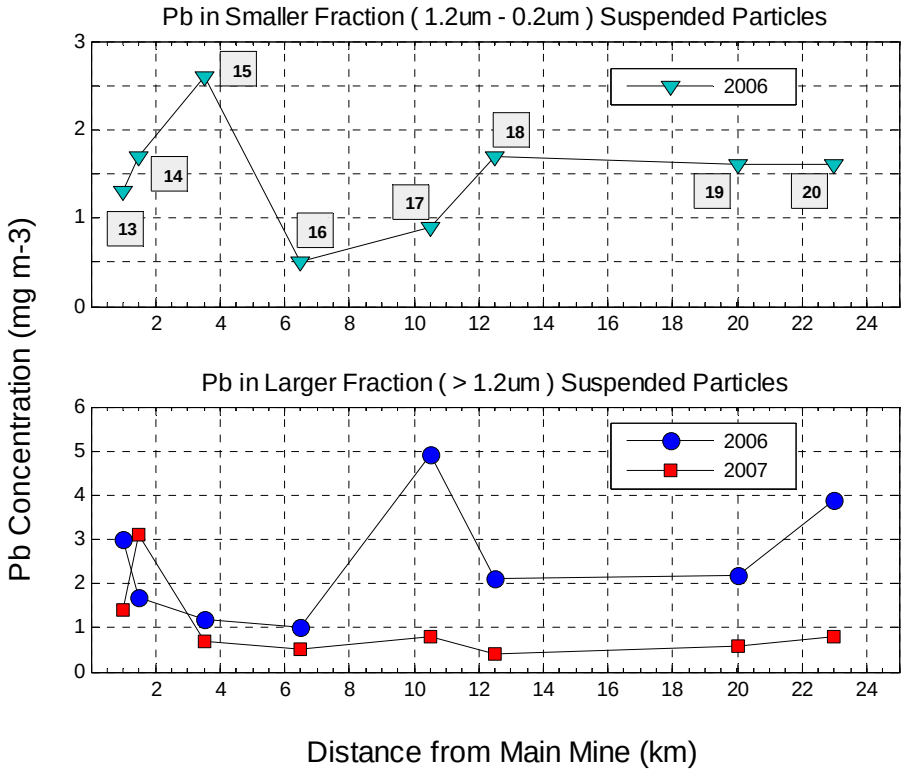


Figure 4.22: Pb in Suspended Particles from Water 13 – 20

The Pb concentration for the smaller size fraction shows a fairly small range of between 0.5 mg m^{-3} and 2.5 mg m^{-3}. The concentration displays an increasing trend at the earlier locations with a peak at Water 15, after which a very low concentration of 0.5 mg m^3 was detected at Water 16. The concentration then starts to increase again upon entering the lakes at Water 17 and 18. The presence of Pb within this size fraction remains constant from this point onwards.

The larger size fraction (1.2μm – 0.2μm), displays a slightly wider range of Pb concentration between 0.5 mg m^{-3} and 5 mg m^{-3}. The samples collected in 2006 show a gradual decrease from location 13 through 16. An increase in Pb is then observed at the first lake at Water 17. The concentration then reduces slightly at the next lake, Water 18 and remains at similar concentration levels with Water 19. The Pb within the suspended particles then increases at the last location, Water 20. The 2007 samples on the other hand depict a less irregular concentration throughout the sampling points. Apart from a high peak of 3 mg m^{-3} at Water 14, the trend for this batch reveals a low and an almost constant concentration not exceeding 1 mg m^{-3} of Pb.

The Pb concentration measured within the suspended particles in this section reveals the presence of a slightly higher range of Pb as compared to the solution phase measured previously. As observed on both size fractions, the peaks or increase in Pb at several sampling location suggests the possibility of additional sources along the river system that is not related from the mine at Tyndrum. This can also be observed within the two lakes where both size fractions collected in 2006, show evidence of additional Pb concentration when entering Waters 17 and 18. Nevertheless, it is also noted that the concentration at Waters 18 and 19 displays constant Pb on both sampling occasions and size fractions. Overall, the river system downstream from Tyndrum mine reveals significant amount of Pb being transported within its suspended particles.

The investigation continued with characterisation of the Pb based on its isotopic composition in an attempt to determine the origin of Pb within the suspended particles. Figure 4.23 displays the results of the $^{206}Pb/^{207}Pb$ against the $^{208}Pb/^{207}Pb$. It includes the Pb atom ratio for the suspended particles for each batch of samples as well as atom ratio for Petrol (1.09), Geological Pb (1.168) and Pb from the mine waste in Tyndrum (1.144).

The graph clearly reveals that all of the suspended particles are dominantly consistent with the Pb from the mine site at Tyndrum being the dominant source, with minor inputs from petrol and geological bedrock. This further supports the suggestion by Farmer et al. (1997a) that the waste from the Tyndrum mine site is being transported within the fluvial system.

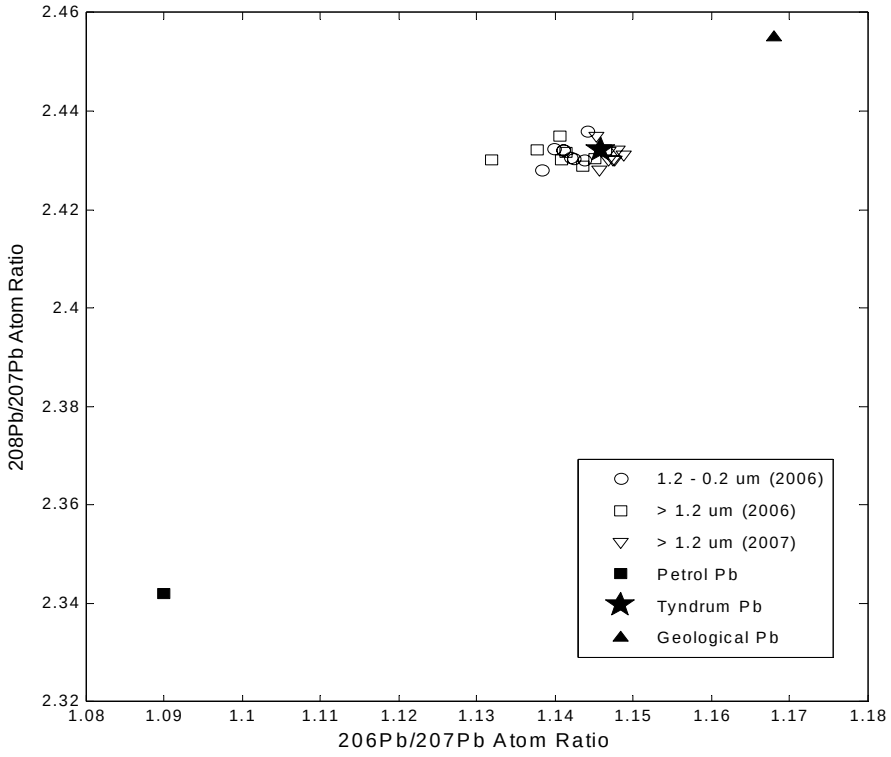


Figure 4.23 The Atom Ratio of $^{206}Pb/^{207}Pb$ against $^{208}Pb/^{207}Pb$ for Suspended Particles, Petrol, Tyndrum Pb and Geological Pb

Based on data from the Centre for Ecology and Hydrology National River Flow Archive, the River Dochart at Killin has a mean flow of 16 m^3 sec^{-1}. Referring to the results in the < 0.2 µm fraction, there is about 1.6 mg Pb m^{-3} of water and 3.8 mg Pb m^{-3} in the 0.2 – 1.2 µm fraction. Taking the Pb loads in the two fractions given above, and the mean flow, it was found that approximately 800 kg Pb per year is transported in the < 0.2 µm fraction, and 1950 kg Pb per year in the 0.2 – 1.2 µm fraction. This shows that there is a considerable amount of lead transported by the River Dochart to Loch Tay. This lends support to the suggestion by Farmer et al. (1997a) concerning the transport of Pb from Tyndrum to Loch Tay.

The suspended particles were also analysed for Zn and include both size fractions collected from the 2006 and 2007 batch of samples. Figure 4.24 shows that the lower size fraction samples had an overall range between 0.3 mg m^{-3} and 6 mg m^{-3}. Both sets of samples, from 2006 and 2007, show a decrease in Zn concentration upon leaving the main mine at Water 13 through Water 16. The concentration for the 2006 sample then shows a steep rise at the lake location of Water 17, but the 2007 sample shows a much smaller increase here. The Zn concentration then levels to an almost constant rate throughout location 18 through 20. This is evident on both sets of samples. Apart from Water 17, the other locations reveal very little influence from other sources throughout the fluvial system. Overall, the Zn concentration within this size fraction displays a gradual decrease as the river system leaves the Tyndrum main mine.

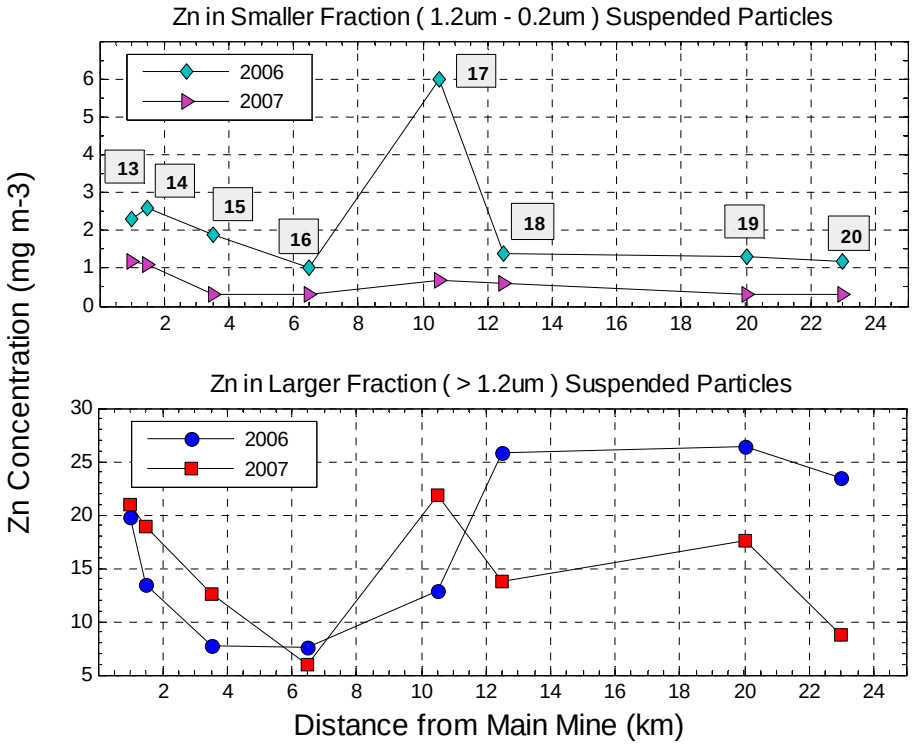


Figure 4.24: Zn in suspended particles from Water 13 – 20

The larger size fraction on the other hand, displays a much higher range of approximately 5 mg m^{-3} to 27 mg m^{-3} of Zn concentration for both sets of samples. The Zn concentration trend for both 2006 and 2007 samples, similarly display a sharp decrease from Water 13 to 16. As expected, the Zn concentration then rises as it enters into the two lakes with a maximum of 22 mg m^{-3} at Water 17 and a maximum of 26 mg m^{-3} at Water 18. This supports the previous Pb data and the suggestion that there exists an additional input within these locations. The concentration trend then displays an almost constant level as observed previously, between location 18 and 19. The level of Zn then shows a decrease as it enters the last location at Water 20.

The extremely high Zn measurement at point 17, which refers to Loch Dochart, is reflected not only in this batch of samples but in the overall Zn concentration results of both size fractions. The Zn concentration results also reveal that the suspended solids at the higher fractions contain more Zn. It can be assumed that Zn is being transported mainly within the > 1.2 μm size fractions of the suspended particles.

Using the mean flow of 16 m^3 sec^{-1} for River Dochart at Killin, it was found that approximately 600 kg Zn is transferred within the < 0.2 μm fraction in a year. The larger fraction displayed an even higher transport of Zn within the waters with 11,600 kg Zn per year. This was calculated according to the Zn concentrations taken in 2006, where the lower fraction has about 1.2 mg Zn m^{-3} and the higher fractions with 23 mg Zn m^{-3}. As similarly found with the Pb results, there are also extensive amount of Zn being carried within the river system and distributed along its tributaries.

Based on the overall results of the suspended particles, both Pb and Zn reveal several comparable trends. Generally, there is a similar decrease throughout point 13 to 16, suggesting metal weathering or sedimentation process of the suspended materials along the river system. The metal concentration however is greatly enriched upon entering the lakes especially at Water 17, Loch Dochart. This could indicate a possible source of metal dispersal nearby.

Another observation that was similar between Pb and Zn was the remarkably constant concentration at Water 18, Loch Lubhair right up to the river at Water 19. Considering the long distance between the two locations, which measures approximately 7.5 km in length, the metal concentration does not reveal any indication of weathering. This could probably signify that the metals are constantly moving along the river in suspension and experiencing very low sedimentation. Stronger currents are probably produced due to the fluvial system leaving a wider lake and entering a narrower river system.

Generally, the results in this section have revealed that there is a considerable amount of metal within the suspended materials being dispersed away from the mine. As mentioned earlier in Section 2.2.3, Buffle & Leppard (1995) gave an explanation of the characteristics of aquatic colloids and macromolecules to better understand their role as carriers of trace compound. Colloids will form unstable suspensions due to their tendency to undergo conformational changes, aggregate, and then sediment. As reported by Zhang et al. (2004) heavy metals in river water 30 km downstream of a Pb-Zn mine in Guizhou China, rapidly reached background level, whereas Pb and Zn contents in the sediment at the same distance are still very high. The study concludes that the heavy metals migrate along with suspended matter and then settle down into sediment. It suggests that characterising mine tailing effects within surface waters are more effectively indicated from sediments. Thus, to give a wider understanding on the dispersal process from the Tyndrum mine site, the investigation of this study continued with the analyses of metal within the sediment materials along the river.

4.3.3 Riverbed Sediments

The riverbed sediment samples were analysed to define the metal concentrations in the different size fractions, namely coarse sand (> 180 μm), fine sand (53-180 μm) and silt and clay (< 53 μm). The objective was to investigate differences in movement of different sediment size fractions and any influence of this on subsequent deposition of metals in the riverbed. Such processes could be of importance in explaining the mechanism of heavy metal fluvial dispersal from Tyndrum. The results obtained for Pb concentrations in the riverbed sediment are shown in Figure 4.25. There are a wide range of Pb concentrations for both batches of samples, with values between 20 mg kg-1 and 7000 mg kg-1. There is also a steep decreasing trend with increasing distance downstream of the river system from sampling point 13 to 16. The concentration then gradually levels off for the rest of the other sampling points. Apart from a slight increase at Water 18 (2007), the decreasing trend is observed in both 2006 and 2007.

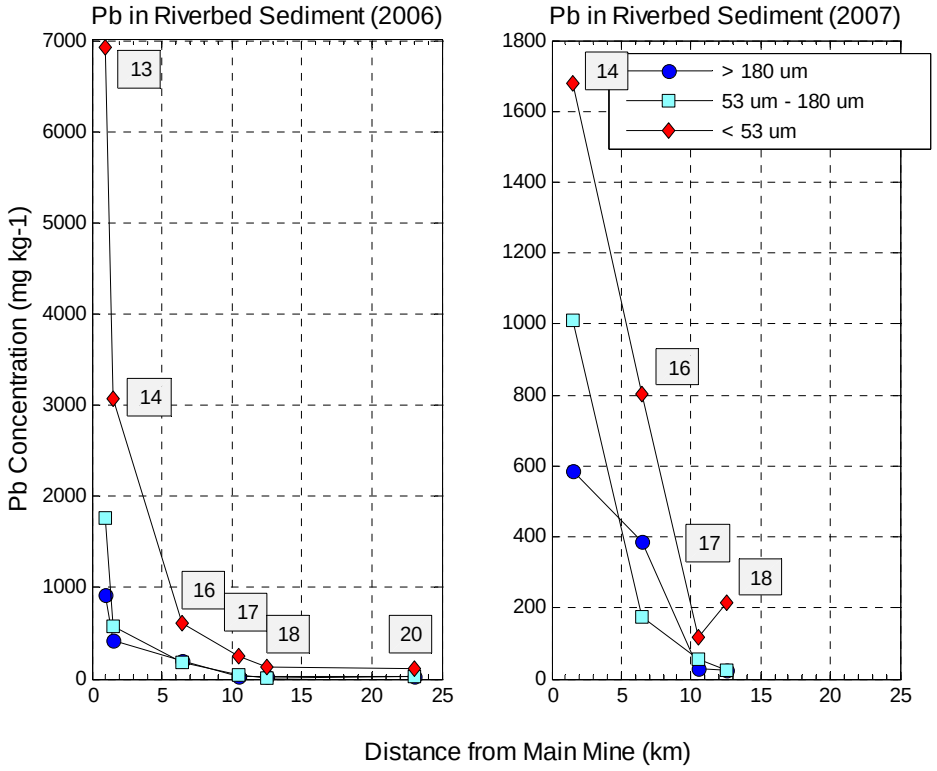


Figure 4.25: Pb concentrations in Riverbed Sediment

Another apparent observation is the Pb concentration within the different size fractions of the riverbed sediments. It was found that Pb concentration decreased much slower throughout the sampling points in the less than 53 μm size fraction. This was evident throughout all of the sampling points in both the 2006 and 2007 samples. Sediments of this size are easily transported and displaced by water flow especially in the events of high currents. As pointed out by Horowitz & Elrick (1987) as grain size decreases thus increasing its surface area, trace element levels also increase. The study found the correlation between grain size and trace element greater within the < 63 μm or < 125 μm fractions. This is also compatible with the suggestion by MacKenzie and Pulford (2002) that there is significant fluvial transport of particulate waste in the less than 53 μm size range.

Unfractionated riverbed sediments were also analysed for $^{206}Pb/^{207}Pb$ and $^{208}Pb/^{207}Pb$ isotopic composition to categorize the origin of Pb in the samples. As shown in Figure 4.26, the isotopic ratio of Petrol, Geological Pb and Tyndrum Pb are included. The isotope ratio of the samples lies between 'petrol' and 'geological' values. This reflects that the sediments represent a mixture of the two, with Tyndrum Pb being the dominant component. As before, this observation is also consistent with the isotopic data presented by Farmer et al. (1997a), implying dispersion of Tyndrum waste as far as Loch Tay. It is also interesting to note that the ratio is relatively constant for the four samples, irrespective of distance from the source.

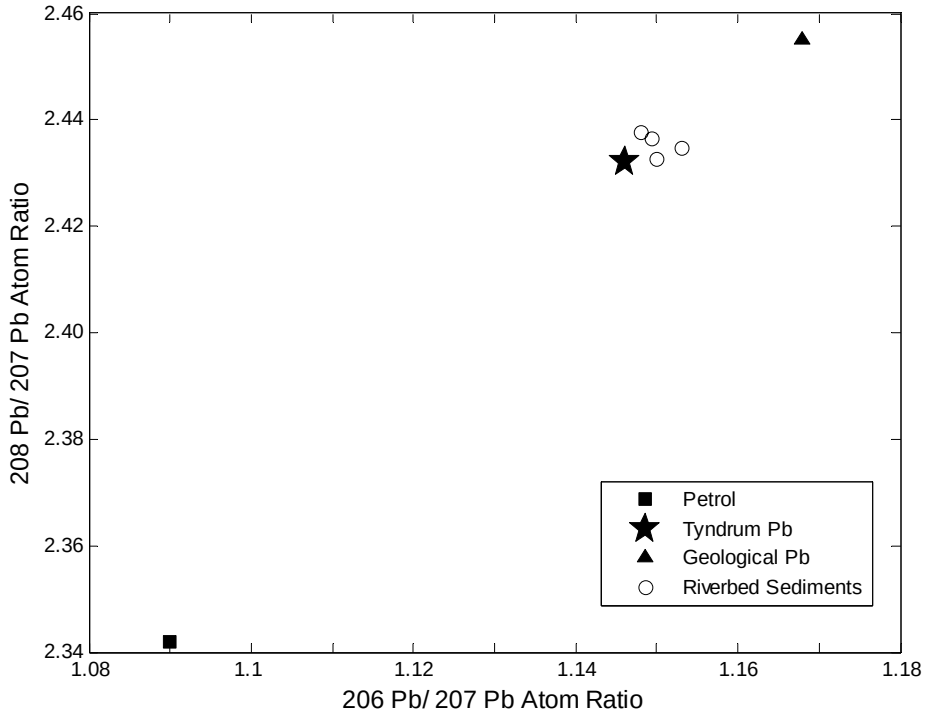


Figure 4.26 : The Atom Ratio of 206Pb/207Pb against 208Pb/207Pb for Riverbed Sediments, Petrol, Tyndrum Pb and Geological Pb

The Zn results for the riverbed sediments are shown in Figure 4.27. The Zn concentrations for both batches of samples were found to be similar within the relatively wide range in 2006 of 40 – 900 mg kg^{-1} and for 2007 of 70- 850 mg kg^{-1}. In 2006, the Zn concentration showed a steep decrease between sampling points 13 and 17 for all of the size fractions. The concentration then gradually levels off for the rest of the sampling locations. The less than 53 μm fraction had the highest Zn concentration, as previously observed for Pb.

The 2007 batch had similar trends to those observed in 2006, with a sharp decrease at the beginning followed by a gradual decrease at points 17 and 18, despite the fact that only four sampling locations were used in 2007. The size fraction between 180 μm – 53 μm had the highest concentration at location 14 with a value of 850 mg kg^{-1}. However, this was only observed at this particular point and the other samples show the less than 53 μm size fraction having highest Zn concentration.

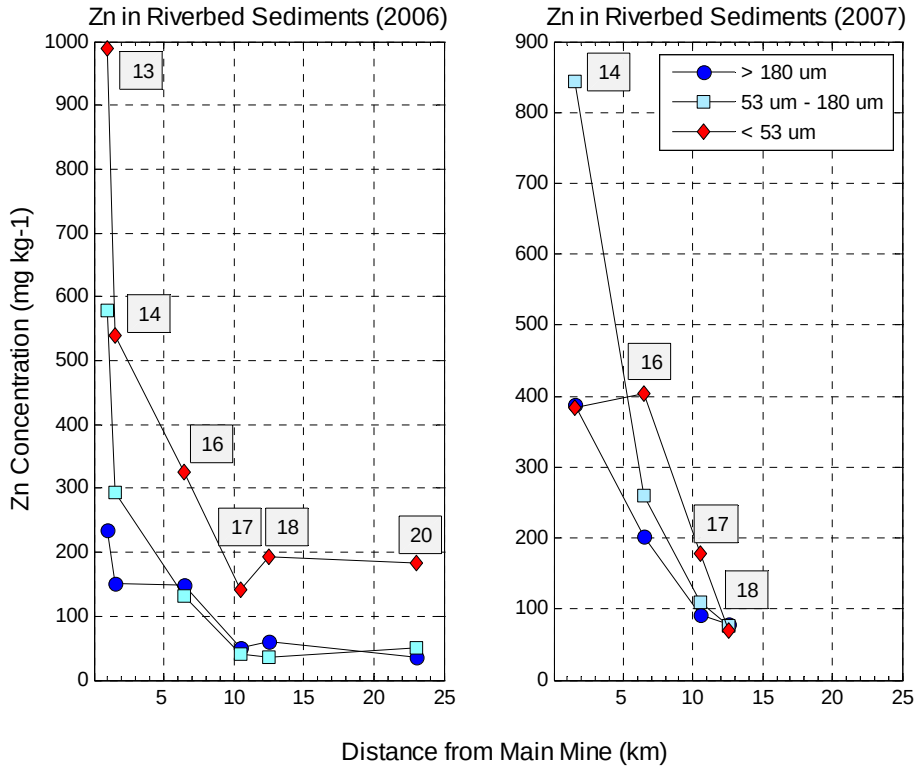


Figure 4.27: Zn concentrations in Riverbed Sediments

The Zn results have demonstrated yet again that the silt and clay fraction plays an important part in the movement of heavy metals within the water body. Similarly observed for Pb, the results have given support to substantiate that the less than 53 μm fraction is an important factor responsible for the heavy metal movement downstream. Being of fine size, this material would undeniably be susceptible to constant movement within the water, especially during the occurrence of storms or strong currents.

4.3.4 Riverbank Core

The results for the analyses of the riverbank core for both Pb and Zn are shown in Figure 4.28. Pb concentration ranged between 18 and 40 mg kg^{-1} while Zn concentration in the riverbank sediments ranged between 45 - 70 mg kg^{-1}. The concentration values are a lower range than those found in the riverbed sediments probably because sediments of overbank cores consist of coarser sediment than the riverbed or suspended sediments.

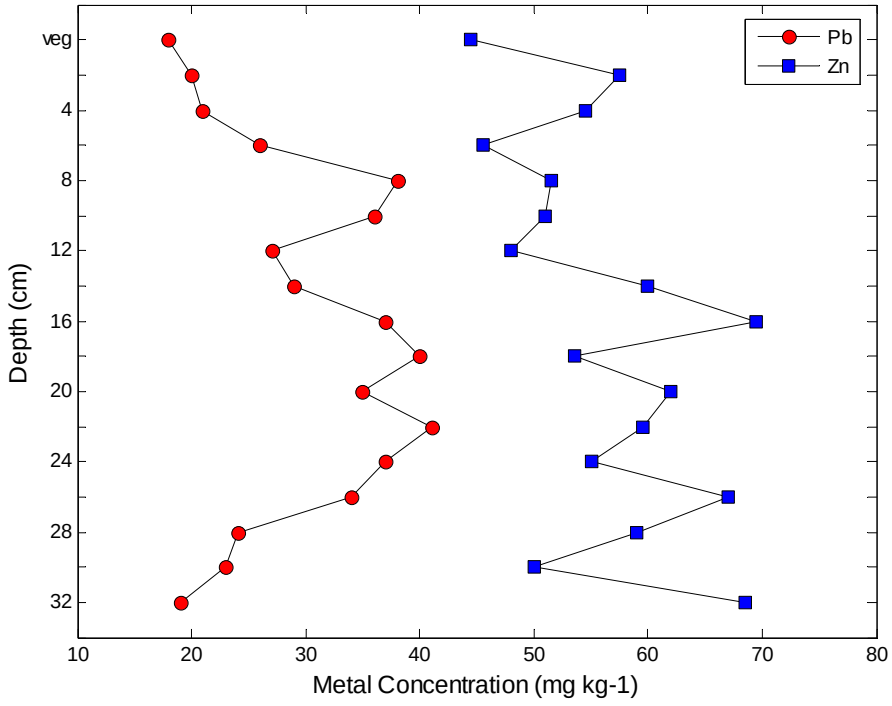


Figure 4.28: Pb and Zn concentration in riverbank core

The Pb profile reveals a gradual increase in concentration below surface levels from about 20 mg kg^{-1} to a peak of 40 mg kg^{-1} at 8 cm depth. The concentration then reduces to 26 mg kg^{-1} at a depth of 12 cm below which the concentration increases with peaks of about 40 mg kg^{-1} at 15 cm and 21 cm depth where a slight reduction in concentration occurs between the two levels.

The Zn concentration profile also demonstrates several peaks throughout the riverbank cores. The layer below the vegetation shows the first peak at 1-2 cm depth of almost 60 mg kg^{-1} before it steadily decreases. At 16 cm depth, a second peak with a maximum concentration of 70 mg kg^{-1} was displayed, below which the value decreases again. The concentration then rose to another two peaks of 67 mg kg^{-1} and 69 mg kg^{-1} at 25 cm and 32 cm depth respectively. Overall, Zn displays irregular peaks throughout the 32 cm core profile. Interestingly the peaks reach almost similar concentration levels of around 70 mg kg^{-1} each. Generally, the Zn concentration trend fails to display any distinct dispersal patterns due to its irregular concentration. A possible mixing or Zn mobility between the different levels may have caused this condition. Zn also reveals much higher concentration range compared to Pb within the riverbank cores.

The riverbank core was analyzed using gamma spectrometry for ^{210}Pb and ^{137}Cs activities in an attempt to determine the sediment accumulation rate for the purpose of reconstructing Pb deposition chronology. The two uppermost layers that consist of some vegetation were not included in the study. The variation in the ^{210}Pb profile indicates variations in sedimentation rate, which means that it is not ideal for the application of the CIC dating model. However, since there are problems with application of the CRS model due to limitations in evaluating the total inventory of ^{210}Pb, the CIC model was used. Thus, the derived sedimentation rate represents the average of the varying rates implied by the ^{210}Pb profile. The sedimentation rate was determined from the gradient of the ln of unsupported ^{210}Pb values plotted versus depth of the riverbank core (Figure 4.29). By applying the ^{210}Pb-dating calculations, the sedimentation rate was found to be at 0.33 cm y^{-1}.

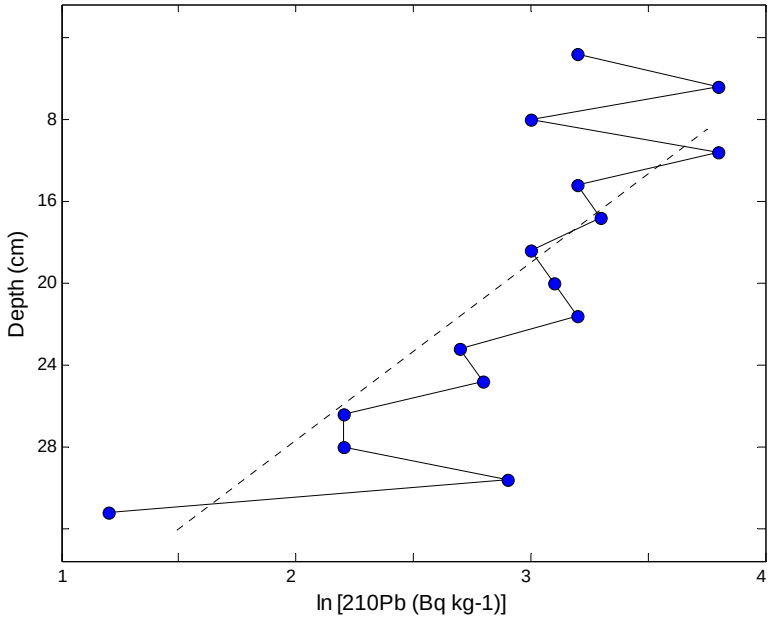


Figure 4.29: ln ^{210}Pb (Bq kg-1) plotted against depth (cm)

As previously mentioned in section 2.2.1, cesium-137 (^{137}Cs) was also measured together by gamma spectrometry to provide an independent check on the ^{210}Pb chronology (Benoit & Rozan (2001)). The initiation onset of detectable ^{137}Cs should correlate to the period of nuclear testing which started in 1952 although is generally not taken as a good chronological marker since it is well established that ^{137}Cs is subjected to downward movement in sediment. Usually, ^{137}Cs can often be detected at depths corresponding to deposition long before the start of the nuclear era. In contrast, diffusion of ^{137}Cs may alter peak shapes but will not alter the position of peaks due to large inputs in 1963 and 1986 (Baskaran et al. (1996); Novotny (2002);Appleby et al. (1988); Edgington & Robbins (1976); Smith et al. (1997)). Based on the time scale for reaching these activities and its corresponding depths, the sedimentation rate was observed as 0.34 cm y^{-1} and 0.30 cm y^{-1}. This closely supports the sedimentation rate calculated using the ^{210}Pb-dating method of 0.33 cm y^{-1}.

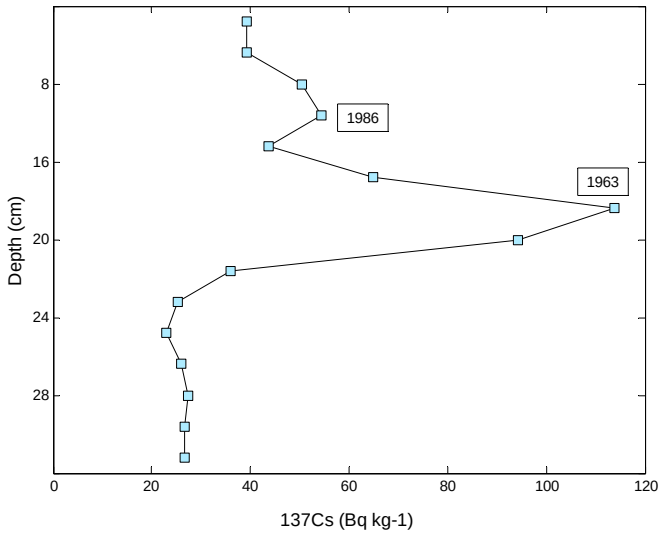


Figure 4.30: 137 Cs activities in riverbank core

The corresponding dates of the riverbank core based on the ^{210}Pb-dating method and the ^{137}Cs marker are as shown in Figure 4.31. The ^{137}Cs dates of 1986 and 1963 correspond very closely to 1983 and 1968 for ^{210}Pb-dating, respectively. The profiles of the dating marker ^{137}Cs and the agreement with the ^{210}Pb predicted dates seemed fairly acceptable and show that the riverbank sediment is largely intact and contain dependable historical inputs. The results have also demonstrated the agreement of applying independent dating marker such as ^{137} Cs to validate the ^{210}Pb chronology.

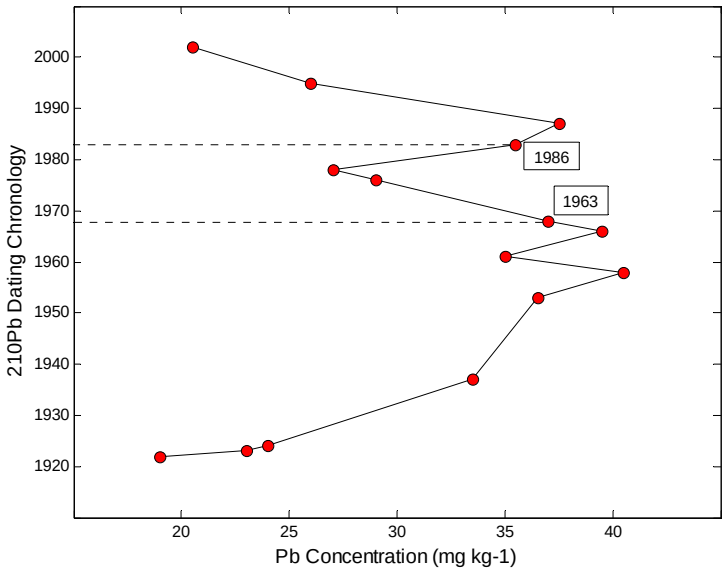


Figure 4.31: ^{210}Pb Dating Chronology with 137Cs Dating (in box)

The characterization of the Pb in the core sediments was also carried out using the Pb isotope ratio of ^{206}Pb/^{207}Pb and ^{208}Pb/^{207}Pb. The atom ratio for the riverbank core is as shown in Figure 4.32. The results depicts that the samples are situated between petrol and geological Pb, although primarily consistent with Tyndrum Pb. The results have thus identified the presence of Pb within the lake system as dominantly of Tyndrum source.

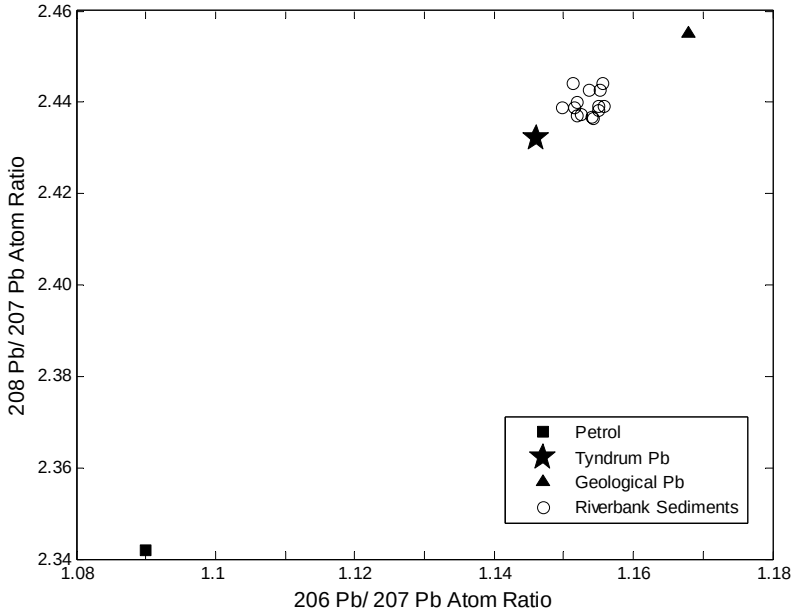


Figure 4.32: The Atom Ratio of $^{206}Pb/^{207}Pb$ against $^{208}Pb/^{207}Pb$ for Riverbank Core

Based on the isotope ratio results, the isotopic fraction between Tyndrum Pb (1.144) and geological Pb (1.168) were calculated against the Pb concentration data to reflect the amount of Pb deposition from the riverbank core by assuming that Pb from other sources such as petrol is negligible.

Figure 4.33 depicts the Pb deposition derived from the isotopic fraction of Tyndrum Pb and Geological Pb as a function of time, based on the ^{210}Pb core dating. The Tyndrum Pb reveals a maximum Pb deposition of approximately 112 mg m^{-2} y^{-1} in the 1930s, possibly corresponding to the re-working of the mine between 1916 and 1925 (Pattrick (1985)). The deposition then reduces until another smaller peak is revealed in the 1960s after which a constant reduction is observed. The trend is strikingly similar to that of the work by Farmer et al. (1997a), which shows the excess Pb flux peaking to about 120 mg kg^{-1} in early 1920s as shown in Figure 2.11. The geological Pb was found to remain almost constant between 10 to 30 mg m^{-2} y^{-1} throughout.

The result interestingly reveals the deposition trend of Tyndrum Pb, which sees a maximum deposition early 1920s –1930s before going though a constant reduction throughout the years to the end of the 20th century. The trend may suggest a decline in Tyndrum Pb dispersal within the water system through time. This assumption however, will require further support, possibly from future investigation work from the site.

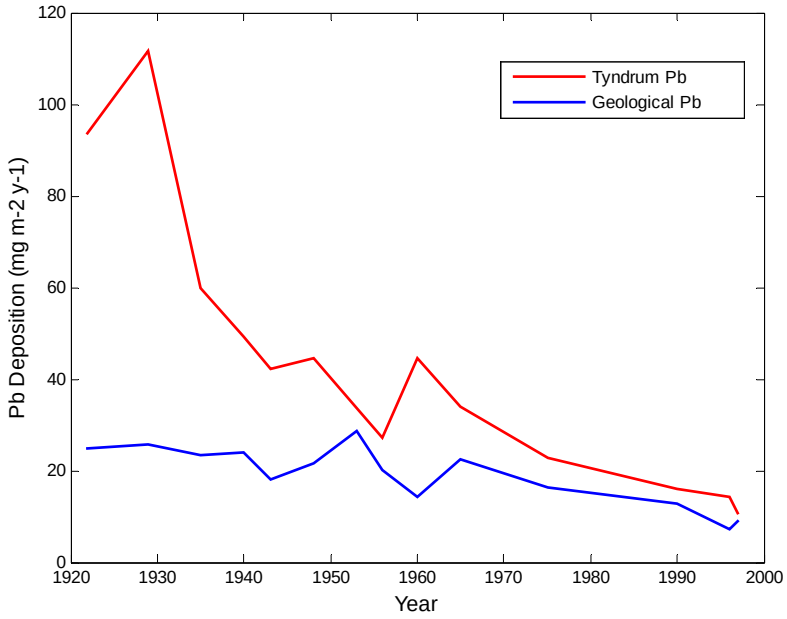


Figure 4.33: Tyndrum Pb Deposition (mg m^{-2} y^{-1}) based on Pb isotope ratio fractions of Tyndrum and Geological Pb versus calendar year.

4.3.5 Summary

The analyses of river water and sediment have provided an overview of the distribution of Pb and Zn within the Tyndrum mine site and downstream. The concentration range measured within the various phases is as shown in Table 4.

Table 4.1: The Concentration of Pb and Zn in Various Phases

Concentration in Various Phases	**Pb**	**Zn**
Solution / Dissolve Phase (mg l^{-1})	0.3 – 2.0	0.2 – 2.5
Suspended Particle – Small Fraction (mg m^{-3})	0.5 – 2.5	0.2 – 6.0
Suspended Particle – Larger Fraction (mg m^{-3})	0.5 – 5.0	5.0 - 25
Riverbed Sediment (mg kg^{-1})	20 - 7000	40 - 900
Riverbank Sediment (mg kg^{-1})	18 - 40	45 - 70

The results show the influence of the former mine towards the river where high levels of Pb and Zn concentration were measured at various points within the main mine compared to concentrations at locations prior to entering the mine. This shows that the mine wastes are the primary source of heavy metal contamination within the river system. The Pb and Zn are also found being transported in suspension downstream from Tyndrum mine site. The heavy metals within the particles, however, did not reveal any reduction in concentration or weathering effect as it moves further away from the point source. This may show possible metal contribution from other sources along the river. Nevertheless, the Pb isotope ratios reveal that the Pb within the suspended particles was dominantly of Tyndrum origin.

The Pb and Zn concentrations within the riverbed sediments were high confirming that the bed sediments act as a sink for heavy metals, although this sink is likely to be temporary in nature due to the continuous movement of bed sediment. The metal concentration displayed a reduction trend with increased distance from Tyndrum main mine with the < 53 μm size fraction decreasing the least. This fraction shows its capability in transporting heavy metals to far distances from its origins.

The riverbank sediments on the other hand revealed several peaks, showing periods of high deposition for both Pb and Zn within the overbank core. The timeline for the contaminant Pb deposition was established using the ^{210}Pb dating method and validated using ^{137}Cs marker. The riverbank and riverbed sediments were both characterised using Pb isotope ratios and the Pb present was found to be mainly of Tyndrum source. The deposition of Tyndrum Pb based on the isotopic fraction saw a constant reduction through time as shown in Figure 4.33, suggesting possible decline in its contribution within the waters. However, further investigation and additional samples in future work is suggested to support this finding.

The investigation on the dissolved, suspended and sediment phases offers additional information and understanding on the movement and behaviour of heavy metals within the water body. The results also demonstrate that the fluvial system is one of the major modes of dispersing and transporting heavy metal contaminants from the former mine site in Tyndrum. Once released into the river, heavy metals will persist in the environment as the complexity and nature of the aquatic environment as an open system is continuously in motion and allows it to spread to far distances.

CHAPTER FIVE

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5.0 CASE STUDY ON THE REMEDIATION OF AN EX-MINING SITE AT BIDOR, MALAYSIA

5.1 Introduction

In the 1960's Malaysia was one of the world's leading producers of tin accounting for about 31 percent of the world's output. However, the tin mining industry collapsed over the last 15 years due to exhaustion of tin deposits, low tin prices and high operating costs. There are about 114 000 ha of former mining area which includes sandy tin tailings as well as slurry ponds (Ang (1994)). The un-treated sites are used extensively for agriculture, aquaculture and growing crops. However, studies have shown that crops grown on these former mining sites have high levels of arsenic, mercury, cadmium and lead (Ho et al. (2000); Mohd Osman & Ang (1999)). Fish bred in ex-mining ponds were also found to contain PTEs, which when absorbed into human bodies can cause kidney and liver failure as well as cancer (Ang et al. (2000)).

Currently, under the mandate of the State Government, appropriate systems have been developed for rehabilitation of these contaminated lands. Research is presently conducted by the Forest Research Institute Malaysia (FRIM), to improve the site quality of tin tailings through remediation techniques such as planting forestry systems. On-going studies on the extent of heavy metal dispersal are also continuously being conducted on designated sites.

The case study in Bidor provides a comprehensive scope on how contaminated ex-mining sites are being managed in a country outside Britain. This study focuses on two main phases, literature survey and experimental work. The literature survey will be explained in section 5.2, which looks into several research reports as well as a general summary of the management and usage of former tin mining sites in Malaysia. The experimental work will be explained in the following section 5.4, followed by the results. Some discussions and conclusions will be addressed in subsection 5.4.2.

5.2 Tin Mining in Malaysia

This section covers the first part of the case study. It looks into several literatures and reports by researchers that are presented from various aspects regarding the situation of former tin mining land in Malaysia. This includes investigation on contamination levels of tin tailings, PTEs found in soil and food production that is grown on tin tailings as well as a rehabilitation project currently being done by FRIM at a research station in Bidor.

5.2.1 Background

Tin mining is Malaysia's well-known legacy and begun its active debut late nineteenth century immediately after the British colonization of Malaya. Beginning in the north and stretching southward through the main range of the peninsula, these activities have resulted in about 113 700 ha of former mining land also known as tin tailings. The most extensive sites are concentrated in the state of Perak (63%) followed by Selangor (22%) (Ang (1994)). Calls for land reclamation of these devastated areas however, are nothing new and has been of concern by various authorities and private individuals since the colonial era. One of the most recorded efforts was in 1951, when a grant was awarded from the Colonial Development and Welfare Fund (Mitchell (1957)). The purpose of this fund was to conduct research and find means of rehabilitation by introducing site-improving tree species or what is known today as 'Afforestation'. Rehabilitation work continues at present by various research institutions namely the Forest Research Institute Malaysia (FRIM).

5.2.2 Impact of Tin mining

Tin mining activities have resulted in the destruction of plants and animals, as well as the topography and pose a health risk to humans. As cited by Shamshuddin et al. (1986), river beds become shallower, drainage systems experience silt and agricultural land contaminated due to previous mine work. Former mining lands or better known as tin-tailing areas, are also known to have low water holding capacity, high hydraulic conductivity, low nutrient status and poor structural stability. Mitchell (1957) also mentioned inevitable results of tin mining are slurry ponds, which can range from a few hectares to several square kilometres in size. They are filled with tailings, rainwater, garbage, sand, clay and silt up to a depth of 40 metres. The condition of former mines poses an immense environmental impact and safety risk to the surroundings. Former mine sites are also surrounded by large slurry ponds and subjected to erosion, which makes it unsuitable for property development.

Tin mining land would usually undergo extensive change in its physical as well as chemical properties due to the methods employed in extracting the tin ores. In Malaysia, tin is obtained from alluvial tin deposits using gravel pump, dredging and opencast mines. These methods employ water for the mechanical separation of the tin ore from the tin-bearing soils. Due to this process, the topsoil is lost and the clay and silt washed away. This result in sandy tin tailings made up of coarse and fine sand. Mitchell (1957) reports that tin tailings will continue to lose clay content to erosion for a prolonged duration after the dumping process. This reduces the chance of land reuse for agriculture as sandy tin tailings have low organic content, low water retention as well as being acidic. Only small pockets of such infertile sites are used for settlement, vegetable farming and fruit tree growing. Large amounts of fertilizer are required to reclaim this land for agriculture. Site improvement methods have to be introduced before a particular site is to be reused to counter the effects of previous mining activities. The cost is prohibitive, and consequently large tracts of tin tailings remain idle.

Potentially Toxic Elements in Food Crops

There are about 4730 ha of tin tailings currently being used for food production in Malaysia (Ang (1994)). Recently, crops cultivated on tin tailings have been found to contain alarming levels of PTEs. Places like Bidor, which once relied economically on its mining activities are now extensively utilizing its ex-mining sites for agriculture. Crops such as mango, guava, water-apple, sweet potato, and vegetables are important daily produce from the locality. Fish that are bred in slurry ponds and mine pools are also not excluded from PTEs, as reported by Ang & Ng (2000); Ho et al. (2000); Mohd Osman & Ang (1999). Research on some economically important fish such as *Tilapia mossambica* has found to contain alarming levels of arsenic (As), mercury (Hg), cadmium (Cd) and lead (Pb). Ang et al. (2000) reported that the concentration of Pb, Cd and Hg in crops and fish has exceeded the permissible limits of the Food Acts 1983 and Regulations 1985 as shown in Table 5.1.

Table 5.1: Heavy Metals in Crops, Water and Tailings on Tin Mines

Ang & Ng (2000); Ho et al. (2000)

Parameters	**Cd**	**Zn**	**Pb**	**As**
Vegetables	1.43	35.86	7.0	0.98
Fruits	0.12	8.74	8.71	
Fish (mine pool)	NA	NA	2.0	0.20
***Permissible Limits**	1.0	3.5	0.5	0.1
****Ground Water**	NA	1.2(0.4)	0.1(0.02)	1.7(0.4)

Notes:
*Food Act 1983 and Food Act Regulations1985 (MDC 1996).

**Value in brackets denotes permissible limits from DOE (1996)

All values are in $mgkg^{-1}$ dried weight.

NA – Not Available

Sources of Potentially Toxic Elements in Ground Water

Extremely high levels of As, Pb and Hg can be detected in the ground water of idle tin tailings and surface water in Bidor. As reported by Ang & Ho (1994), all of the PTEs had exceeded the permissible limits of river water as stipulated by the Department of Environment (DOE) 1996. Hence, the potential of ground water or surface water from sand tin tailings in Bidor to be exploited as drinking water is limited. The presence of PTEs in the ground water was from the fine sediments of tin tailings. According to Mohd Osman & Ang (1999), the PTEs are mainly derived from geological formation, e.g. Pb derived from galena (PbS) and cerussite ($PbCO_3$), As derived from arsenopyrites (FeAsS) and cobaltite (CoAsS), and Hg derived from alluvial cinnabar (HgS). Adding fertilizers to enhance organic levels of soils also could have caused an increase in the PTE levels. At plots where biosolids are used as organic fertilisers concentrations of As, Zn, Pb and Hg would have accumulated the PTEs through leaching or seepage.

5.2.3 Utilization of Former Tin Mines

In a developing country like Malaysia, the utilization of mining land is unavoidable. In fact, its capital city Kuala Lumpur originated from one of the first tin mining town in the peninsula. Currently due to the country's vast infrastructure, which includes roads, railway lines, buildings, houses even skyscrapers are built on and around former mine land as well as mining ponds that have been refilled and reinforced. Generally, the utilization of former tin mining areas can be divided into three major usages: housing and property development, agriculture and aquaculture, as well as recreational purposes.

Housing and Property

In major cities such as Kuala Lumpur and Ipoh, land is much needed for its rapid development. With the country's agenda of reaching a developed country status in the year 2020, there are increasing demands for modern infrastructure. Hence, mining land is not excluded from being incorporated by the government for the development of the country. This includes building of roads and highways, railway lines, industrial and manufacturing sites as well as commercial and private properties. Engineers, town planners and property developers have for years, successfully built towns and cities on former mining land. Nevertheless, development on former tin mine sites has not been easy and has its setbacks and problems. Due to past mine workings, former tin mine sites mostly contain weak soil structures with predominant sandy soils (Shamshuddin et al. (1986)).

Building solid structures on ex-mining land therefore, requires a lot of piling and restructuring work to ensure its resistance and endurance against erosion or cave-ins. There have been cases where buildings and roads experience fracture due to weak structures and flawed construction. This proves to be an unwelcome health and safety hazard. However, over the years the building construction industries has developed and is constantly improving building technologies that are reliable in ensuring safety as well as quality in its build. The government has also set stringent rules and regulations where buildings have to be approved fit by experts before it is occupied.

Recreation

Another example of a successful development of a mining area is at a place known as Seri Kembangan, which initially was a small tin mining town in the 1960's. It is now transformed into a small township which boasts a prestigious five-star hotel set at the edge of a large mining pool, a water marina, a theme park, a large mall surrounded with sprawling acres of housing areas with schools and offices. Looking at its impressive facade, many would have forgotten its legacy if not for its name, aptly known as 'The Mines'.

Recreational clubs and resorts have always been a favourable choice for the development of former mine sites as it gives higher economic value per land area compared to private housing or agriculture use. Most former mining pools in the town area are now turned into water recreational park such as the Tasik Titiwangsa in Kuala Lumpur.

Agriculture and Aquaculture

Generally, the usage of a mining area will depend on its geographic locality. Most former mines situated near large towns and cities are focused on property development and recreation purposes as it is in high demand. However, former mine land in rural areas are mostly used for agriculture and aquaculture. Most of these lands are owned by the government and are leased out to farmers. Although faced with infertile soil and sandy tin tailings, the farmers have over the years successfully grown crops and vegetables using fertilizers and enhancers. Former tin mining pools are also put to use with breeding a vast variety of fish species. However, recent findings by researchers as mentioned in Section 6.2, causes much concern, as it involves consumable products from these sites that directly enters the food chain. Due to these alarming reports, various research institutions are now looking into ways to remediate and reclaim the contaminated mine lands. An alternative would be introducing timber related trees that have economical value. This would be a beneficial move as it will not only protect the consumers from buying tainted food produce but also gives the farmer an alternative to continue with its livelihood.

5.2.4 Remediation Effort - Afforestation

The state government mostly owns tin mines in Malaysia. The mines are then leased out to private mining companies. According to Mohd Rafek (1985), The Mining Enactment F. M. S. Cap.147 does not specifically deal with rehabilitation of mining land. Miners are only required under section 5(i) of the mining enactment to fill and level with no rise of ground steeper than 1 vertical to 18 horizontal and without standing water. Usually the miners themselves do not carry out the rehabilitation practice because in most cases the tenure of the mining lease is too short for any proper mining by the companies. This creates a lot of mines being left untreated and abandoned. Yeong (1985) suggested that a fund for the rehabilitation of mining land should be established for Government projects as and when the need arises. This would ensure that the mining lands are not left idle and derelict, as the land can be use economically for property development and agriculture.

About 80% of tin tailings is sand and the rest is slime and sandy slime (Shamshuddin et al. (1986)). Slime consists of clay and silt, found in localities previously used as detention ponds for discharged tailings, and is better ground for agriculture than sand as it has good drainage. Sand is very infertile and is not suitable for cultivation. The low percentage of clay in tin tailings makes any form of planting efforts difficult because it reduces the cation exchange capacity (CEC) and water holding capacity of the tin tailings (Mitchell (1957)).

In areas where dredge mining was used, it is common practice to ensure that much of the coarse sand and gravel is subsequently covered with silt clay, a practice known as sliming. This type of land is much more amendable to reclamation by forestry (Mitchell (1957)). As reported by Mohd Rafek (1985), tree planting on tin tailing is recognised to be an effective rehabilitation method.

One of the most important aspects of planting trees on ex-mining tin areas is that it initiates natural succession by modifying the micro-environment by reducing evaporation of the soil by shading effects and contributing the organic matter on the top soil (Koter & Nuruddin (2004)). Several potential tree species have been identified and reported by Mitchell (1957) and Ang (1994) that can be planted to improve the site.

Land reclamation efforts of tin mine land has been conducted since the early 1950's. Mitchell (1957) reported of a research project funded by the Colonial Development and Welfare Fund to conduct research and find means of rehabilitation by introducing site-improving tree species or afforestation. The Forest Research Institute Malaysia (FRIM) is currently one of the active institutions undertaking rehabilitation works. The next paragraph will look into the research centre for afforestation work in Bidor.

Bidor Research Centre

In July 1996, the State Government of Perak, (PSG) sanctioned an area of 121.4 ha of ex-mining land in Bidor to FRIM for the establishment of a research station. The urgent need for greening the tin tailings with useful tree species have been acknowledged and endorsed by policy makers and the government. The tin tailings at the site consists of slime and sand tailings that are predominantly covered by grass and sparsely colonised by several pioneer species such as *Muntingia calabura, Vitex pubescens,* and *Mallotus* species.

The FRIM research station is actively developing appropriate forestry systems for rehabilitation of degraded lands. Amongst its main objectives are to carry out research in developing cost effective tree planting techniques on tin tailings, to conduct research in improving the site quality and to generate financial gains from utilisation of the former mine site.

5.3 Aim of Case Study

This research study looks into the former tin mining site at Bidor. Based on the work done in Tyndrum, Scotland, it is hoped that the study will provide interesting insight of the two former mine sites that is different logistically but of a similar nature. The aim of the two-month study at FRIM aims to achieve the following;

1. To conduct a literature survey on the general management of former tin mining site in a country outside United Kingdom

2. To quantify the extent of atmospheric dispersal of heavy metals on ex-mining sites from bark samples of timber species

5.4 Investigation of Atmospheric Dispersal at FRIM Research Station

As previously mentioned, the experimental work is the second and final part that concludes the overall research study at FRIM. As described in the following paragraphs, the experimental work involves sampling of a former tin mine site at the Bidor research station. The samples were then analysed at the FRIM laboratory according to the methodology mentioned.

5.4.1 Sampling and Methodology

The sampling site is at a former tin mining land in Bidor (4°06'N latitude, 101°16'E longitude), a mining town about 128 km north of Kuala Lumpur. It is located about 6 kilometres northwest of Bidor town and covers large tracts of ex-mining land. Topographical features found were waterlogged areas, tailing heap, farmland, ponds, dry ditches, flowing drains and sand tracks. The uncultivated areas were predominantly bushes and shrubs, which consisted of grasses, legumes, ferns, and herbaceous plants typically found on tin tailings (Mohd Osman & Ang (1999)).

In order to quantify the extent of atmospheric dispersal of heavy metals, samples from tree bark are analysed. This will give an overview of the contamination levels dispersed through the atmosphere at the former tin mining site.

The research station consists of many different tree species that are planted at different parts of the area. Bark samples were collected on 10th January 2007 from three different tree species that differ in distance to an untreated mine area on the other side of the FRIM's boundary, as shown in Figure 5.1. The three different tree species are: *Acacia auriculiformis* (AA), *Mahogani swietenia* (MS) and *Hopea ordorata* (HO). An additional sample was also taken from an *Acacia hybrid sp*. (R) situated within a dense forest area for the purpose of background or remote sample.

Bark is extracted at a height of 1.5 m on an approximately 15x15 cm area, using a penknife. Samples are taken on the southeast sides or directly facing the untreated site. Samples taken from the sampling site are placed in self-sealed bags and labelled. Upon returning to the laboratory, the samples were initially air-dried in room temperature. The air-dried samples are placed in the oven at a temperature of 110^{o}C for about four hours to constant weight. The dried samples were then pulverised to uniform size with a laboratory mill. The mill was thoroughly cleaned and dried after each grinding to avoid contamination between samples. About 2 g of accurately weighed powdered sample was then transferred into a vitrosil crucible and pre-ashed until the fumes disappeared. It was then transferred into a muffle furnace and ashed at 450^{o}C for 4 hours.

A single sample is ashed in triplicate to test the reproducibility of the method used. The ash was then dissolved with 1.6M HNO_3 solution and filtered into a 100 ml standard volumetric flask. The digests were then made up to mark with 1.6M HNO_3. The samples were analysed for Pb and Zn using the Varian Septra, AA10 Atomic Absorption Spectrophotometers at the Ecophysiology Laboratory at FRIM.

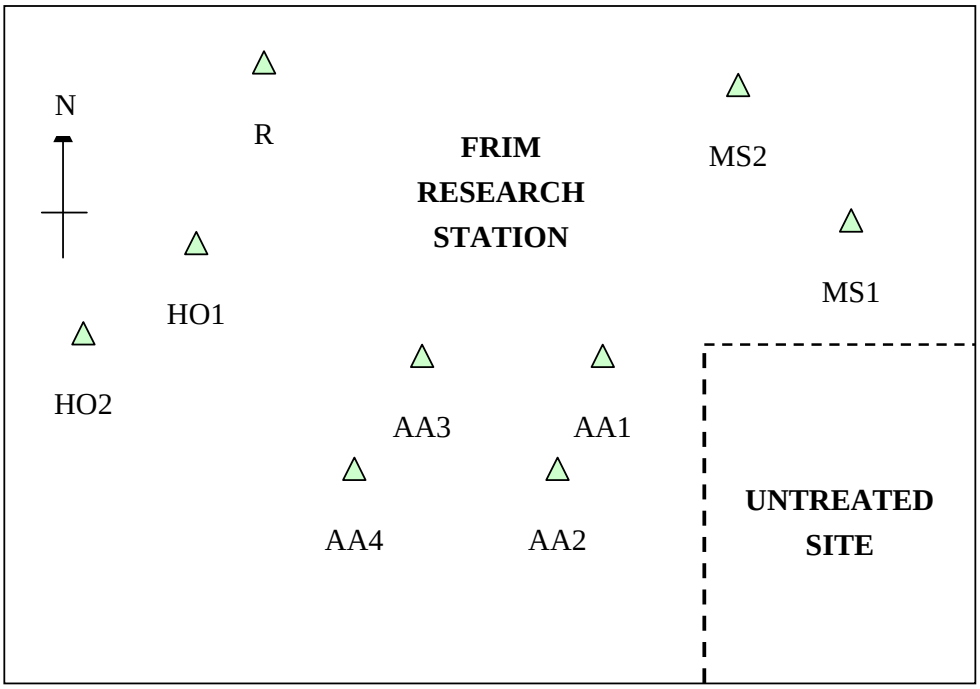

Figure 5.1: Sampling location of tree bark at FRIM

5.4.2 Result and Discussion

The results of the analyses are as shown in

Figure 5.2. The tree species are arranged according to estimated distance from the boundary of the untreated site, where MS1 is closest to the boundary and R (remote) sample is farthest.

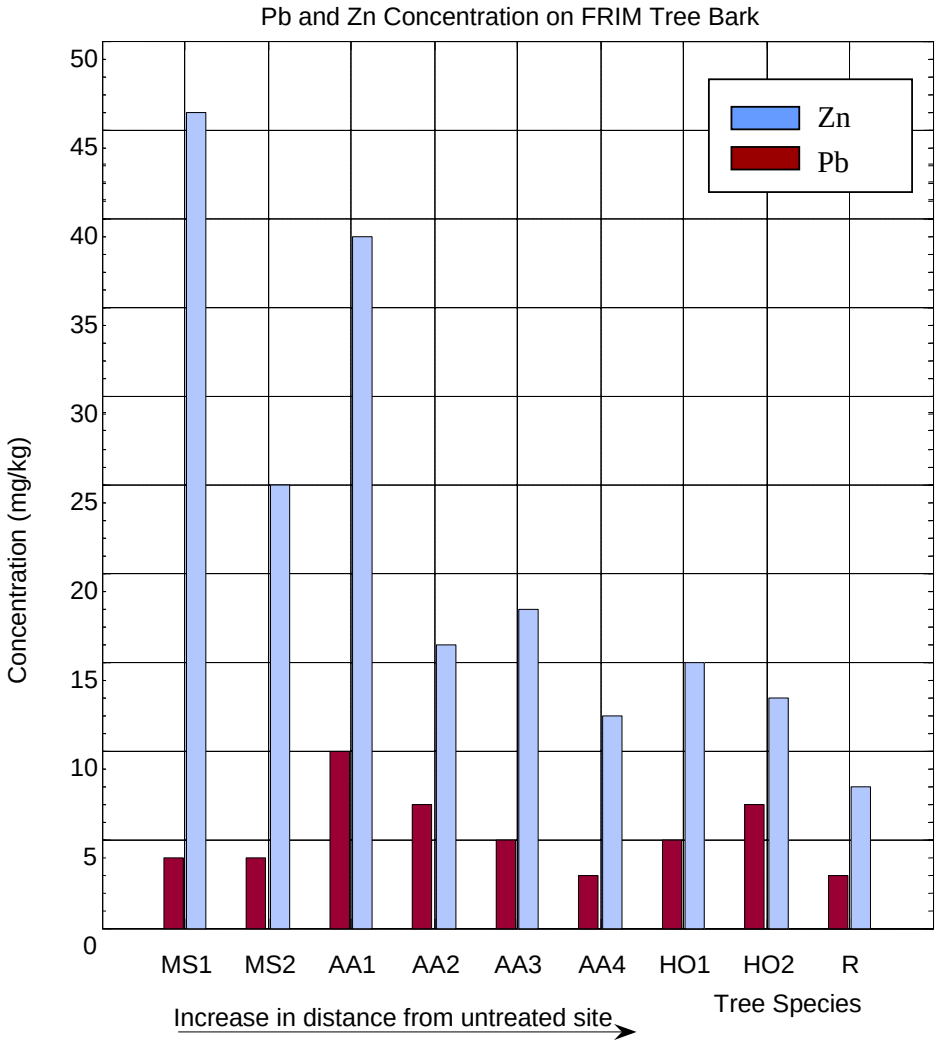

Figure 5.2: Pb and Zn Concentration on FRIM Tree Bark

The concentration result for the three different bark species had a range of between 3 $mgkg^{-1}$ – 10 $mgkg^{-1}$ for Pb and 12 $mgkg^{-1}$ – 46 $mgkg^{-1}$ for Zn concentration. The bark collected from the tree species at the remote area showed the lowest concentration of 3 $mgkg^{-1}$ and 8 $mgkg^{-1}$ of Pb and Zn respectively.

The small range of Pb concentrations disclose an almost even level with very little variability between each of the tree bark samples. The Pb results are thus assumed to reflect the state of atmospheric dispersal within the treated site, as there are no past records of atmospheric deposition on site. The Pb results also do not display any relation of concentration with distance from the boundary of the untreated site. Although the bark collected from the remote area did accumulate the lowest Pb concentration compared to the rest at 3 $mgkg^{-1}$, the differences between the other barks are very slight. Hence, differences based on distance to the untreated site will be dismissed. However, the result does reveal a striking resemblance to the measurements of Ho et al. (2000), which reported 11.3 $mgkg^{-1}$ of Pb concentration on surfaces of idle tin tailings on another ex-mine site about 50 km away. Taken into account that the barks in FRIM were taken on sides facing the untreated area, the measured values might reveal possible atmospheric deposition blown from the surface of the neighbouring untreated site onto the bark surfaces. This assumption however, will require further studies such as tree barks on different side facing aspects, as carried out at Tyndrum, Scotland.

The Zn results alternatively display higher level of concentration with a wider range between the samples. Unlike the Pb measurements, Zn results exhibit a decreasing trend with increased distance from the boundary of the untreated area. This implies the correlation of higher exposure of trees that are at closer distance from a contaminant source. In this case, the source would be the untreated site surrounding the boundary of FRIM. This trend corresponds with the trend measured from tree bark at Tyndrum, which also displays a decrease in concentration with increased distance.

The ratio of Zn/Pb, as shown in Figure 5.3 displays higher ratio for trees MS 1 and MS 2, which is closer to the untreated site. The rest of the trees show an average Zn/Pb ratio of 3. It can be suggested that the airborne particles may contain similar ratio of the contaminants observed on the tree bark surfaces. However, comparisons cannot be made at present due to lack of reference on the waste particles of the former mining site.

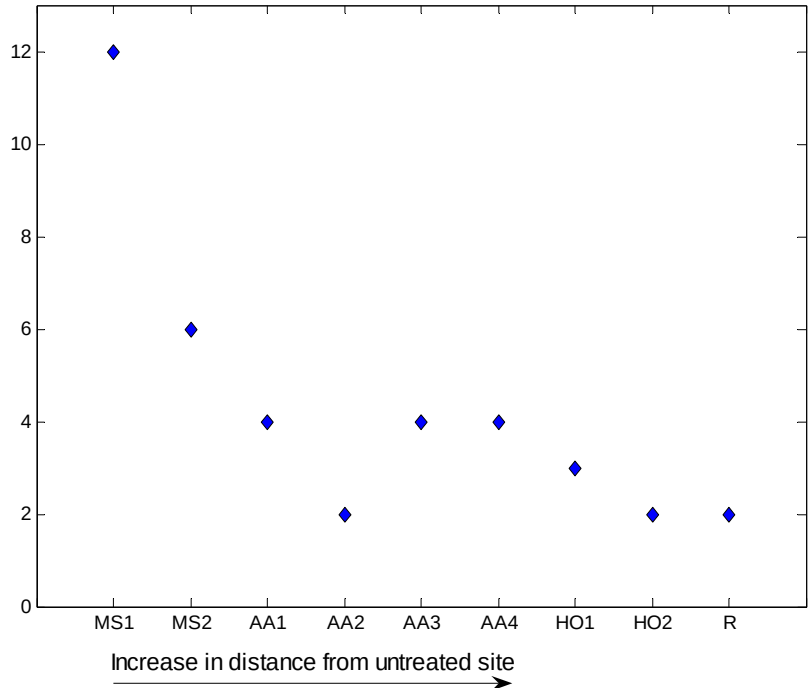

Figure 5.3: Zn/Pb Ratio

5.5 Summary of Case Study

The overall results display the feasible use of bark samples from *Acacia auriculiformis* (AA), *Mahogani swietenia* (MS) and *Hopea ordorata* (HO) and proving the occurrence of atmospheric deposition within the mine site. This experiment marks a beginning towards the usage of tree bark samples as indicators for evaluating atmospheric dispersal at FRIM research station. It is recommended that further studies on tree bark be carried out at wider distances as well as at different side aspects for better evaluation of atmospheric dispersal of the site. Although the study had a limited number of samples collected, it has been shown that tree bark provides new and valuable information on the magnitude and source of airborne contamination. Repeat studies at future dates would prove to be interesting.

CHAPTER SIX

6.0 CONCLUSIONS AND RECOMMENDATIONS ***152***

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6.0 CONCLUSIONS AND RECOMMENDATIONS

The main aim of this research study was to investigate the distribution of lead and zinc contaminants in Tyndrum, attributed by its mining legacy through various pathways. Atmospheric dispersal of the contaminants within the mine site was examined from its eventual fallout and deposition on peat profiles and tree bark surfaces. Distribution of contaminants through fluvial transport are assessed from the river system on site and extended downstream about 25 km from the main mine. The research also conducted the characterization of the source of contaminants in the sediment samples brought about by fluvial dispersal using Pb isotope analyses. Past deposition in peat cores and riverbank sediments were also reconstructed by means of the ^{210}Pb-dating method.

The first section of this chapter will explain the conclusion on the overall findings on the tree bark. This will then be followed by conclusions based on peat core analyses and the river water and sediments. This includes the three different phases: solution, colloidal and suspended phase. Several recommendations are also included on possible future work on the subject.

6.1 Tree Bark

The investigation on tree bark was aimed to provide information on the airborne dispersal of contaminants, which has not been attempted before in Tyndrum. Based on the results obtained, it is demonstrated that the elemental analyses of Pb and Zn on the tree bark samples have provided new and valuable information concerning the magnitude of atmospheric contamination at the site.

The first focus of the tree bark investigation was on the concentration levels at various distances from the mine waste. It was concluded that an inverse relation between distance and concentration were found, where with increased distance from the dumpsite, the concentration of the contaminants measured from the tree bark decreased.

The tree bark analyses have also shown that the atmospheric dispersal of the mine waste is contained, in this case within approximately 50 m radius from the Main Waste Dump. Beyond this distance, the concentration is lower possibly due to the density of the tree stand, acting as filters of the airborne dispersal.

In this research study, two sides of a tree were sampled to observe differences on airborne deposition. It was found that the sides directly facing the dumpsites have higher deposition due to greater exposure, compared to its opposite sides. However, at distances further away from the point source, in this case 50 m radius beyond the main dumpsite, the concentration found on both sides did not reveal much difference from one another. This concludes that airborne dispersal does reveal greater concentration on sides directly facing point sources. However, at a further distance from the point source, the differences between both sides tend to decline.

A new approach that was carried out on the tree bark analyses was the investigation of airborne deposition at different heights. It was found that the concentration of contaminants show gradual reduction at increased heights. This was similarly observed on needles, twigs and cone taken at two different heights. Thus, it can be concluded that the airborne contaminants are deposited at increasingly lower concentration as the height increases.

The final analysis on the tree bark was comparing the deposition of contaminants of different aged trees. The results revealed that the concentration was of similar magnitude. It is believed at this point that this is due to the shedding process of the tree bark. Hence, the amount of deposition on bark surfaces regardless of the age of the tree remains similar as it is exposed to similar atmospheric dispersal. This finding also indicates that the concentrations measured on all of the tree bark surfaces are of contemporary origin and that the contaminant from the mine is continuously persistent.

As a conclusion, the use of tree bark in the investigation of atmospheric dispersal was found to be reliable and well suited especially when tree plantation is available at a site of interest. Although the final outcome may seem unlikely to provide an exact quantitative measurement of airborne dispersal, it is likely to prove valuable for rapid identification of areas where the levels of pollution may be of environmental concern.

6.2 Peat Cores

The investigation on peat cores was carried out to reveal the deposition of contaminants via the atmospheric dispersal pathway. The eventual fallout on peat surfaces over time has given information on past atmospheric levels, dated by means of the ^{210}Pb method. The peat cores represent cores nearer the main site, cores 1-4 and further north-northeast from cores 5-8.

The results from the peat core samples 1-4 also known as the Small Side Dump have successfully shown apparent peaks during the early and mid 19th century. This implies substantial activities during these times at the site. The general concentration trend for the cores shows a gradual decline towards the surface, giving the assumption of a steady reduction of atmospheric contamination.

The investigation on cores 5-8 reveals lower concentration ranges than the SSD, as it is situated at a further distance from the main mine. Nevertheless, apart from Core 8, the general trend does reveal a gradual decrease in concentration levels towards the surface of the core. Again, this could imply that the concentration of the contaminants in the atmosphere is gradually reducing. Core 8 on the other hand, seemed to be the only location displaying high Pb at surface levels and higher concentration range of Zn than the rest of the cores. SEM images of particles taken from the depth of 5-6 cm suggest the presence of waste particles from the SSD possibly from past atmospheric deposition.

As a conclusion, the peat core analyses have shown evidence of historical deposition. It is also concluded that the cores show gradual decrease in its concentration towards the upper layers. Although this gives the suggestion of possible reduction of atmospheric contaminants, the abandoned waste dumps may still pose as a source of contamination.

6.3 River Water and Sediments

The River Water and Sediment investigation has been carried out to study the magnitude and movement of Pb and Zn contaminants within the water body in different phases. The results have given information on the behaviour and extent of the Pb and Zn contaminants. In addition to that, the overall results have managed to bridge the gap on the issue of fluvial movement of Tyndrum mine waste dispersing along its tributaries. This refers to past studies, which have shown evidence of Tyndrum waste in Loch Tay by Farmer et al. (1997a). Consequent work at the main mine by MacKenzie and Pulford (2000), had shown significant leaching of the waste within the river sediment.

This research study had managed to connect the two key findings by Farmer and MacKenzie and Pulford, by providing essential evidence into the movements of the mine contaminants via fluvial dispersal between Tyndrum and Loch Tay. The research firstly concludes that the solution phase at the main mine contains relatively low concentrations of Pb and Zn (not exceeding 5 mgl^{-1}). Based on these findings the conclusion is that the heavy metals are mostly within the colloidal phase and less in solution form, which also corroborate well with the theory presented by Kennish (1992).

It was further revealed that the contaminants then continued its journey downstream from the main mine, mostly within the over 1.2 μm fraction. The riverbed sediments show that the contaminant deposits itself throughout the river system, with the < 53 μm containing most of the heavy metals. Based on both results, it is assumed that the contaminants journeyed throughout the fluvial system, from Tyndrum towards Loch Tay, mostly within the 1.2 μm – 53 μm fraction.

In the fluvial movement process, the sediments are consequently deposited on the riverbeds as found in the rivers and lochs. The concentrations of the fractions were also found to decrease with distance possibly due to dilution process by other tributaries or over bank deposition during its movement.

The fluvial study therefore concludes that the transportation of contaminants from the mine is indeed progressive and persistent. Based on the sediment results and utilising data from the Centre for Ecology and Hydrology National River Flow Archive for average flow loading information, it was found that approximately 800 kg Pb and 600 kg Zn is transported in the < 0.2 μm fraction per year, and 1950 kg Pb and 11,600 kg Zn per year in the 0.2 – 1.2 μm fraction.

The $^{206}Pb/^{207}Pb$ isotope ratio revealed Tyndrum as the main contributor of Pb within the suspended particles, riverbed and riverbank sediments. This further strengthens the suggestion of Tyndrum's contribution towards the heavy metal contamination deposited along its river system.

Summary

In general, this research study has managed to provide a comprehensive scope on the extent and magnitude of the fluvial and atmospheric dispersal at the Tyndrum mine waste. The mine's contaminants are evidently transported from the mine through the fluvial system within its colloidal phase. The presence of the contaminants is less influential within the dissolved phase as it appears to be actively transported within the suspended particles. It is thus concluded that the mine waste from Tyndrum is still actively dispersed by the river system where metal bearing sediments are constantly being disposed throughout its path, accumulating in riverbed sediments, lake sediments and riverbanks.

The extent of atmospheric dispersal was found to be severe only within the main mine especially areas close to the Main Waste Dump as shown on the tree bark analyses. The peat core analyses also show high level of deposition that is localised within the mine site. This was evident where high contamination levels of contemporary deposition were only found for cores at the Small Waste Dump. Evidence of Tyndrum waste was found within the 5-6 cm depth in Core 8 may relate to past atmospheric input. Therefore, it is suggested that the high contaminant levels brought about by atmospheric distribution is mostly contained and appears to decrease further away from the site.

6.4 Recommendation for Future Work

The overall research work has provided a general overview on the impact of Tyndrum mine waste towards the environment. Several new investigations were carried out in this research, which has managed to provide new evidence as well as corroborate with past studies. With the completion of this research work however, several proposals and suggestions of possible future work were found to be necessary. The recommendations also include work that can be carried out to reduce the environmental impact of the mine.

The study on the river system reveals that the fluvial route acts as one of the most important and persistent pathways. This route is able to distribute contaminants along its path, transporting contaminants as far as the length of the river system. As suggested by Farmer et al. (1997a), Tyndrum Pb may have travelled 25 km to Loch Tay. It would be interesting to investigate on whether the Pb contaminants are dispersed at locations further away such as the estuaries near the Firth of Tay, where River Tay ends. Identification techniques using stable Pb isotope $^{206}Pb/^{207}Pb$ have been shown reliable in the past and therefore would provide dependable analysis.

The investigation of the atmospheric dispersal had indicated localised contamination of the mine waste. Nevertheless, the condition of the open and sandy waste of the Main Waste Dump has shown to be the main cause of persistent contamination towards the surrounding area. It is recommended that appropriate measures should be taken to cover the open waste dump to reduce further displacement of the waste. In view that the mine site is within public access, such as the West Highland Way, notices of the waste dump should also be placed to warn walkers and travellers of the dumpsite.

The localised conditions of the contaminants were possibly due to the barricade of tree stands planted surrounding the mine area. This has assisted in reducing the distance of atmospheric transport of the contaminants from travelling further from the site. It is of concern however, that there still exists an open area between the mine's dumpsite and the residential area of Tyndrum. The northeast side of the mine is void of any trees or structure that can hinder wind blown particles. The lack of trees at this angle has probably caused for distribution of the contaminants as shown in peat core 8. The exposed waste material thus may travel via airborne transport free from obstruction directly towards the village.

This exposure could contribute to increased Pb exposure via inhalation. Thus, in the interest of human health and safety, it is recommended to undertake further analyses of airborne dispersal at sites in the village and at the same time determine the blood Pb content of residents.

Soil analyses from within the village using Pb isotope ratios could also be carried out to determine the origin of possible Pb content. New plantation of tree stands between the mine and the village can also prove to be valuable in providing an obstruction of the contaminants transport through the atmosphere.

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APPENDIXES

7.0 LIST APPENDIXES

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Appendix 1: Tree Bark

Tree Sample	Pb (mgkg-1)		Zn (mgkg-1)	
	SE	NW	SE	NW
1	22	18	21	15
2	21	22	20	16
3	23	19	20	18
4	22	18	11	21
5	47	20	25	16
6	70	8	19	40
7	34	18	61	44
8	1849	375	141	77
9	64	111	18	25
10	1546	411	118	87
11	1664	334	86	29
12	59	27	31	37
Y	13	21	32	30

Tree Sample	Height (m)	Pb (mgkg-1)		Zn (mgkg-1)	
		SE	NW	SE	NW
X	5	264	42	63	86
	4	794	58	60	101
	3	874	63	54	101
	2	905	111	52	163
	1	935	272	63	169
	0.5	996	1455	184	228
Needles	7m	11	N/A	58	N/A
Twigs	N/A	120		25	
Cones		8		17	
Needles	5m	28	N/A	62	N/A
Twigs	N/A	209		51	
Cones		39		55	

Appendix 2: Pb and Zn in Peat Core

Sample	Depth	Pb	Zn
		(mgkg-1)	(mgkg-1)
Core 1	veg-1	43	156
	1-2	84	86
	2-3	105	71
	3-4	104	91
	4-5	262	99
	5-6	1102	141
	6-7	2611	291
	7-8	3664	453
	8-9	1850	384
	9-10	1115	250
Core 2	veg-1	NA	324
	1-2	892	372
	2-3	853	233
	3-4	1041	247
	4-5	1942	227
	5-6	3203	219
	6-7	4348	370
Core 3	veg-1	1780	933
	1-2	2016	63
	2-3	4648	59
	3-4	1857	64
	4-5	2139	65
	5-6	2799	71
	6-7	4668	458
	7-8	631	315
	8-9	692	354
	9-10	818	328
	10-11	3816	462
	11-12	3490	448
Core 4	veg-1	714	340
	1-2	1214	896
	2-3	268	56
	3-4	260	60
	4-5	1740	75
	5-6	1949	63
	6-7	1820	78

Sample	Depth	Pb	Zn
		(mgkg-1)	(mgkg-1)
Core 5	veg-1	43	76
	1-2	50	94
	2-3	212	107
	3-4	219	62
	4-5	288	52
	5-6	401	40
	6-7	444	99
	7-8	450	54
	8-9	641	63
	9-10	724	58
Core 6	veg-1	51	83
	1-2	83	102
	2-3	407	83
	3-4	824	95
	4-5	537	19
	5-6	574	29
	6-7	640	49
	7-8	789	52
	8-9	927	67
	9-10	1251	70
Core 7	veg-1	76	75
	1-2	250	84
	2-3	36	38
	3-4	23	12
	4-5	26	10
	5-6	22	12
	6-7	20	12
	7-8	5	10
	8-9	2	10
	9-10	1	11
	10-11	1	10
Core 8	veg-1	749	324
	1-2	702	372
	2-3	1429	233
	3-4	320	247
	4-5	305	227
	5-6	256	219
	6-7	526	370
	7-8	310	269
	8-9	300	277

Appendix 3: ^{210}Pb Chronology – Peat Core

Core 1

depth	Pb210	ln(Pb210)	dry weight	mg	mass/area	c. mass	Bq / sctn	Age	Year
0-1	BDL	BDL	35.7	35730	95	47	NA	8.0	1997
1-2	BDL	BDL	35.6	35610	94	142	NA	24.0	1981
2-3	BDL	BDL	46.9	46880	124	251	NA	42.6	1962
3-4	BDL	BDL	35.9	35900	95	360	NA	61.2	1944
4-5	BDL	BDL	42.0	42000	111	463	NA	78.7	1926
5-6	BDL	BDL	38.5	38530	102	570	NA	96.7	1908
6-7	480.7	6.2	56.7	56660	150	696	27.2	118.1	1887
7-8	216.7	5.4	70.6	70560	187	864	15.3	146.7	1858
8-9	61.0	4.1	100.2	100240	265	1090	6.1	185.0	1820
					sed rate = 5.89		Area = 368m2		

Core 2

depth	Pb210	ln(Pb210)	dry weight	mg	mass/area	c. mass	Bq / sctn	Age	Year
0	141.6	5.0	45.7	45700	110	55	4348	5.2	2000
1	250.7	5.5	108.7	108700	263	242	3203	22.7	1982
2	360.2	5.9	75.3	75300	182	464	1942	43.5	1961
3	463.3	6.1	160.9	160900	389	749	1041	70.3	1935
4	569.8	6.3	122.9	122900	297	1092	853	102.4	1903
5	695.7	6.5	218.9	218850	529	1505	892	141.1	1864
					sed rate = 10.664		Area = 414m2		

Core 7

depth	Pb210	ln(Pb210)	dry weight	mg	mass/area	c. mass	Bq / sctn	Age	Year
0	BDL	NA	16.92	16920	195	97.70	NA	0.8	2004
1	BDL	NA	30.53	30530	353	371.69	NA	3.1	2002
2	69.33	4.24	90.03	90030	1040	1067.85	6.24	8.8	1996
3	18.00	2.89	128.83	128830	1488	2331.62	2.32	19.3	1986
4	12.00	2.48	130.39	130390	1506	3828.44	1.56	31.6	1973
5	6.67	1.90	154.30	154300	1782	5472.34	1.03	45.2	1960
6	11.00	2.40	146.50	146500	1692	7209.26	1.61	59.6	1945
7	15.33	2.73	154.81	154810	1788	8949.13	2.37	73.9	1931
8	3.00	1.10	151.25	151250	1747	10716.42	0.45	88.5	1916
9	7.67	2.04	128.80	128800	1487	12333.53	0.99	101.9	1903
10	4.67	1.54	329.17	329170	3801	14978.00	1.54	123.7	1881
					sed rate = 121.055		Area = 86.59m2		

Appendix 4: Pb in Solution, After Filtration (1.2um), After Acidification

Pb Original

Sample/ Batch	1	2	3	4	Average	Stdv
W1	0.62	0.00	0.13	0.99	0.435	0.5
W2	2.66	0.85	0.84	1.77	1.530	0.9
W3	2.89	1.08	2.02	1.94	1.983	0.7
W4	2.38	0.86	2.09	1.71	1.760	0.7
W5	0.87	0.00	0.12	0.22	0.303	0.4
W6	1.56	0.24	0.87	1.51	1.045	0.6
W7	1.41	0.31	1.37	1.40	1.123	0.5
W8	1.54	0.34	1.58	1.45	1.228	0.6
W9	1.90	0.25	2.13	1.46	1.435	0.8
W10	1.56	0.20	1.35	1.64	1.188	0.7
W11	1.08	0.98	1.18	0.78	1.005	0.2
W12	1.51	0.00	1.26	1.11	0.970	0.7

Pb Filtered

Sample/ Batch	1	2	3	4	Average	Stdv
W1	0.61	0.00	0.21	0.33	0.288	0.3
W2	2.61	0.52	1.89	1.94	1.740	0.9
W3	2.94	0.69	2.14	2.08	1.963	0.9
W4	2.35	0.42	1.53	1.93	1.558	0.8
W5	0.86	0.00	0.18	0.51	0.388	0.4
W6	1.51	0.00	1.02	1.59	1.030	0.7
W7	1.67	0.00	1.18	1.73	1.145	0.8
W8	1.57	0.00	1.24	1.77	1.145	0.8
W9	1.73	0.00	1.93	1.72	1.345	0.9
W10	1.59	0.00	1.26	1.72	1.143	0.8
W11	1.10	0.00	1.18	1.09	0.843	0.6
W12	1.53	0.00	1.19	1.18	0.975	0.7

Pb Acid

Sample/ Batch	1	2	3	4	Average	Stdv
W1	0.79	0.70	0.26	0.61	0.590	0.2
W2	2.88	0.43	1.95	2.85	2.028	1.1
W3	3.19	0.88	2.28	3.10	2.363	1.1
W4	2.73	0.52	1.47	2.81	1.883	1.1
W5	0.88	0.00	0.30	1.00	0.545	0.5
W6	2.00	0.13	1.48	2.15	1.440	0.9
W7	1.81	0.18	1.39	2.14	1.380	0.9
W8	1.85	0.20	1.45	2.20	1.425	0.9
W9	1.77	0.16	2.21	2.46	1.650	1.0
W10	1.72	0.74	1.34	2.50	1.575	0.7
W11	2.13	0.00	2.58	1.44	1.538	1.1
W12	1.65	0.00	1.22	1.80	1.168	0.8

Appendix 5: Pb in Suspended Particles

2006 samples

1.2um	Weight (g)	Pb (mg l-1)	Pb (mg kg-1)	Volume (L)	Pb iso	Pb (mg m-3)
W13	0.0037	0.3	4054	5	1.1420	3.0
W14	0.0022	0.17	3864	5	1.1442	1.7
W15	0.0055	0.23	2091	10	1.1410	1.2
W16	0.0026	0.19	3654	10	1.1384	1.0
W17	0.0008	0.97	60625	10	1.1400	4.9
W18	0.0181	0.41	1136	10	1.1438	2.1
W19	0.0113	0.44	1947	10	1.1411	2.2
W20	0.0345	0.77	1116	10	1.1424	3.9

0.2um	Weight (g)	Pb (mg l-1)	Pb (mg kg-1)	Volume (L)	Pb iso	Pb (mg m-3)
W13	0.0028	0.13	2321	5	1.1451	1.3
W14	0.002	0.17	4250	5	1.1436	1.7
W15	0.0075	0.52	3467	10	1.1319	2.6
W16	0.0018	0.09	2500	10	1.1465	0.5
W17	0.0009	0.18	10000	10	1.1414	0.9
W18	0.0583	0.33	283	10	1.1406	1.7
W19	0.0119	0.32	1345	10	1.1408	1.6
W20	0.0319	0.32	502	10	1.1378	1.6

2007 samples

1.2um	Weight (g)	Pb (mg l-1)	Pb (mg kg-1)	Volume (L)	Pb iso	Pb (mg m-3)
W13	0.0028	0.14	2500	5	1.1468	1.4
W14	0.0037	0.31	4189	5	1.1480	3.1
W15	0.0027	0.13	2453	10	1.1458	0.7
W16	0.0015	0.09	3000	10	1.1454	0.5
W17	0.0006	0.16	13333	10	1.1469	0.8
W18	0.0027	0.07	1296	10	1.1488	0.4
W19	0.0032	0.12	1875	10	1.1476	0.6
W20	0.0074	0.16	1081	10	1.1475	0.8

0.2um	Weight (g)	Pb (mg l-1)	Pb (mg kg-1)	Volume (L)	Pb iso	Pb(mg m-3)
W13	0.0018	0.13	3611	5	1.1463	1.3
W14	0.0015	0.10	3333	5	1.1441	1.0
W15	0.0018	0.05	1389	10	1.1453	0.3
W16	0.0005	0.01	1000	10	1.1418	0.1
W17	0.0002	0.03	7500	10	1.1342	0.2
W18	0.0035	0.06	857	10	1.1458	0.3
W19	0.0012	0.04	1667	10	1.1452	0.2
W20	0.0053	0.03	283	10	1.1427	0.2

2007 samples (corrected ICPMS conc)

1.2um	Weight (g)	Pb ICPMS	Pb (mg kg-1)	Volume (L)	Pb(mg m-3)
W13	0.0028	0.269	4804	5	2.69
W14	0.0037	0.348	4703	5	3.48
W15	0.00265	0.115	2170	10	0.58
W16	0.0015	0.117	3893	10	0.58
W17	0.0006	0.137	11417	10	0.69
W18	0.0027	0.127	2348	10	0.63
W19	0.0032	0.132	2063	10	0.66
W20	0.0074	0.140	945	10	0.70

Appendix 6: Zn in Solution, After Filtration (1.2um), After Acidification

Zn Original

Sample/Batch	1	2	3	4	Average	Stdv
W1	0.13	0.00	0.42	0.15	0.175	0.2
W2	1.49	0.62	1.26	1.67	1.260	0.5
W3	1.57	1.27	1.53	2.07	1.610	0.3
W4	1.71	1.20	1.38	1.91	1.550	0.3
W5	0.83	1.36	2.32	1.73	1.560	0.6
W6	1.06	1.39	1.75	1.92	1.530	0.4
W7	1.80	1.57	1.78	1.96	1.778	0.2
W8	0.12	1.93	1.98	2.48	1.628	1.0
W9	0.00	1.87	1.62	1.82	1.328	0.9
W10	1.33	4.12	2.08	2.45	2.495	1.2
W11	0.41	1.20	0.91	1.12	0.910	0.4
W12	1.77	2.62	2.31	2.23	2.233	0.4

Zn Filtered

Sample/Batch	1	2	3	4	Average	Stdv
W1	0.23	0.00	0.27	0.18	0.170	0.1
W2	1.61	0.57	1.54	1.65	1.343	0.5
W3	1.80	0.93	1.99	2.06	1.695	0.5
W4	1.99	1.12	1.45	1.87	1.608	0.4
W5	0.90	1.29	2.83	1.75	1.693	0.8
W6	1.07	1.29	1.12	1.92	1.350	0.4
W7	2.00	1.48	1.76	1.99	1.808	0.2
W8	2.67	1.91	2.51	2.55	2.410	0.3
W9	1.21	1.81	1.39	1.85	1.565	0.3
W10	2.32	3.70	2.21	2.48	2.678	0.7
W11	2.00	1.15	0.00	1.09	1.060	0.8
W12	2.79	2.24	2.15	2.28	2.365	0.3

Zn Acid

Sample/Batch	1	2	3	4	Average	Stdv
W1	0.20	0.00	0.18	0.27	0.163	0.1
W2	1.61	0.59	1.23	1.85	1.320	0.5
W3	1.95	1.28	1.54	2.42	1.798	0.5
W4	1.90	1.16	1.42	2.11	1.648	0.4
W5	1.44	1.34	2.27	2.03	1.770	0.5
W6	1.80	1.19	1.69	2.06	1.685	0.4
W7	2.13	1.48	2.14	2.14	1.973	0.3
W8	2.64	1.94	2.45	2.71	2.435	0.3
W9	2.25	1.90	1.63	1.97	1.938	0.3
W10	2.40	4.23	2.19	2.65	2.868	0.9
W11	2.33	0.71	0.00	1.21	1.063	1.0
W12	2.88	2.54	2.34	2.36	2.530	0.3

Appendix 7: Zn in Suspended Particles

2006 samples

1.2um	Weight (g)	Zn (mg l-1)	Zn (mg kg-1)	Volume (L)	Zn (mg m-3)
W13	0.0037	1.9800	2676	5	19.8
W14	0.0022	1.3500	3068	5	13.5
W15	0.0055	1.5400	1400	10	7.7
W16	0.0026	1.5100	2904	10	7.6
W17	0.0008	1.5500	9687	10	7.8
W18	0.0181	5.1500	1427	10	25.8
W19	0.0113	5.2700	2332	10	26.4
W20	0.0345	4.6800	678	10	23.4

0.2um	Weight (g)	Zn (mg l-1)	Zn (mg kg-1)	Volume (L)	Zn (mg m-3)
W13	0.0028	0.23	411	5	2.3
W14	0.002	0.26	650	5	2.6
W15	0.0075	0.37	247	10	1.9
W16	0.0018	0.20	556	10	1.0
W17	0.0009	1.19	6611	10	6.0
W18	0.0583	0.28	24	10	1.4
W19	0.0119	0.25	105	10	1.3
W20	0.0319	0.24	38	10	1.2

2007 samples

1.2um	Weight (g)	Zn (mg l-1)	Zn (mg kg-1)	Volume (L)	Zn (mg m-3)
W13	0.0028	2.09	3732	5	20.9
W14	0.0037	1.89	2554	5	18.9
W15	0.00265	2.51	4736	10	12.6
W16	0.0015	1.17	3900	10	5.9
W17	0.0006	4.37	36417	10	21.9
W18	0.0027	2.74	5074	10	13.7
W19	0.0032	3.51	5484	10	17.6
W20	0.0074	1.74	1176	10	8.7

0.2um	Weight (g)	Zn (mg l-1)	Zn (mg kg-1)	Volume (L)	Zn (mg m-3)
W13	0.0018	0.12	3333	5	1.2
W14	0.0015	0.11	3667	5	1.1
W15	0.0018	0.06	1667	10	0.3
W16	0.0005	0.06	6000	10	0.3
W17	0.0002	0.14	35000	10	0.7
W18	0.0035	0.12	1714	10	0.6
W19	0.0012	0.06	2500	10	0.3
W20	0.0053	0.06	566	10	0.3

Appendix 8: Pb and Zn in Riverbed Sediments

2006

Pb	> 180 um	180-53um	< 53um
W13	915.5	1755	6920
W14	417.5	581.5	3070
W15	na	na	na
W16	201	180.5	611
W17	25	48	254
W18	29	10	136
W19	na	na	na
W20	28.5	23	118

2007

Pb	> 180 um	180-53um	< 53um
W13	na	na	na
W14	587	1012	1678
W15	na	na	na
W16	385	175	803
W17	27	56	119
W18	23	26	213
W19	na	na	na
W20	na	na	na

2006

Zn	> 180 um	180-53um	< 53um
W13	235.5	578	990
W14	152	292.5	540
W15	na	na	na
W16	147.5	132	326
W17	51	41	142
W18	59	35.5	192
W19	na	na	na
W20	36	51	182

2007

Zn	> 180 um	180-53um	< 53um
W13	0	0	0
W14	387	843	383
W15	na	na	na
W16	203	259	403
W17	92	110	178
W18	79	76	70
W19	na	na	na
W20	na	na	na

Appendix 9: Pb Isotope Ratio

Suspended Particles (2006)

1.2um	206/207	208/207	208/206
W13	1.1420	2.4357	2.1325
W14	1.1442	2.4362	2.1289
W15	1.1410	2.4269	2.1267
W16	1.1384	2.4449	2.1476
W17	1.1400	2.4451	2.1448
W18	1.1438	2.4382	2.1313
W19	1.1411	2.4412	2.1394
W20	1.1424	2.4409	2.1367

Riverbed Sediment (2007)

	206/207	208/207	208/206
W14	1.1530	2.4349	2.1115
W16	1.1479	2.4376	2.1224
W17	1.1500	2.4328	2.1152
W18	1.1494	2.4366	2.1196

Suspended Particles (2006)

0.2um	206/207	208/207	208/206
W13	1.1451	2.4324	2.1238
W14	1.1436	2.4286	2.1233
W15	1.1319	2.4221	2.1396
W16	1.1465	2.4440	2.1318
W17	1.1414	2.4370	2.1348
W18	1.1406	2.4352	2.1345
W19	1.1408	2.4387	2.1378
W20	1.1378	2.4325	2.1378

Suspended Particles (2007)

1.2um	206/207	208/207	208/206
W13	1.1468	2.4306	2.1191
W14	1.1480	2.4360	2.1216
W15	1.1458	2.4321	2.1222
W16	1.1454	2.4281	2.1195
W17	1.1469	2.4325	2.1205
W18	1.1488	2.4300	2.1149
W19	1.1476	2.4320	2.1188
W20	1.1475	2.4303	2.1177

Riverbank Sediment (2007)

Depth (cm)	206/207	208/207	208/206
4	1.1515	2.4390	2.1177
6	1.1518	2.4371	2.1157
8	1.1525	2.4373	2.1145
10	1.1519	2.4400	2.1180
12	1.1512	2.4442	2.1228
14	1.1556	2.4442	2.1147
16	1.1551	2.4427	2.1144
18	1.1542	2.4366	2.1107
20	1.1498	2.4389	2.1208
22	1.1536	2.4427	2.1172
24	1.1540	2.4369	2.1114
26	1.1549	2.4382	2.1109
28	1.1550	2.4391	2.1114
30	1.1558	2.4393	2.1102

Appendix 10: ^{210}Pb Chronology – Riverbank Core

Riverbank Core

depth	Pb210	ln(Pb210)	dry weight	mg	mass/ area	c. mass	Age	Year
2-4	24	3.18	283	283	2.5	1.3	3.8	2002
4-6	44	3.79	263	263	2.3	3.7	11.2	1995
6-8	21	3.03	308	308	2.8	6.3	18.9	1987
8-10	43	3.76	235	235	2.1	8.7	23.0	1983
10-12	25	3.20	299	299	2.7	11.1	28.3	1978
12-14	27	3.30	270	270	2.4	13.6	30.5	1976
14-16	19	2.96	349	349	3.1	16.4	37.5	1968
16-18	21	3.06	268	268	2.4	19.1	39.7	1966
18-20	24	3.18	256	256	2.3	21.5	44.6	1961
20-22	15	2.72	304	304	2.7	24.0	48.3	1958
22-24	16	2.75	357	357	3.2	26.9	53.3	1953
24-26	9	2.21	293	293	2.6	27.3	69.0	1937
26-28	9	2.23	330	330	2.9	27.7	84.0	1922
28-30	18	2.86	150	150	1.3	27.1	82.1	1924
30-32	3	1.16	240	240	2.1	26.8	81.1	1925